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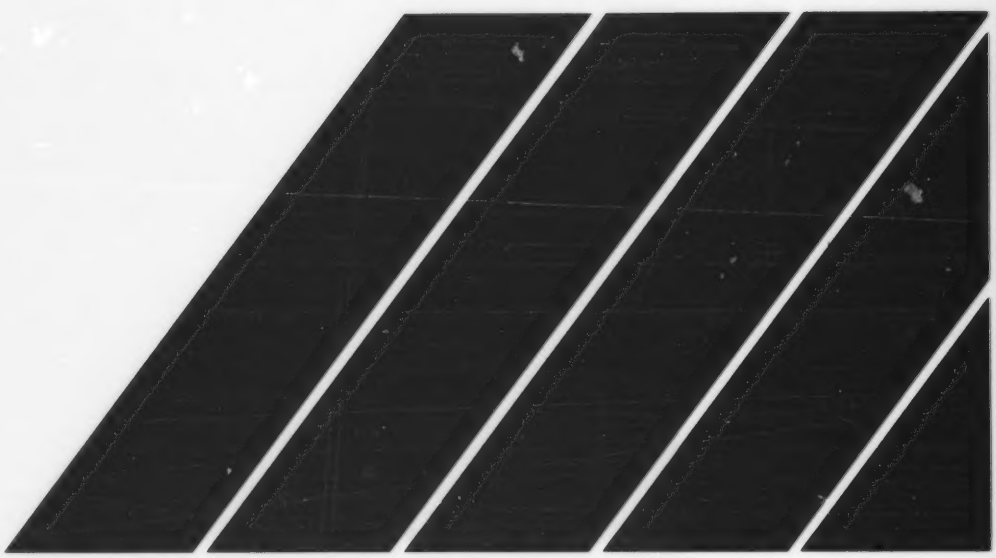
THE USE OF STEAM-EXPLODED LIGNIN IN PLYWOOD ADHESIVES



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THE USE OF STEAM-EXPLODED LIGNIN IN PLYWOOD ADHESIVES

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SUMMARY

This is the final report of "The Use of Steam-Exploded Lignin in Plywood Adhesives" by Iogen Corporation. The lignin used in this work is the byproduct of wood-to-ethanol processing; it is derived from wood that has been rapidly steam-treated (steam explosion), followed by digestion by cellulase enzymes. This lignin was used as a substitute for phenol formaldehyde (PF) resin, the key component in plywood glue formulations.

Lignin was tested in an unmodified (UM) form and after chemical reaction with formaldehyde (hydroxymethylation), phenol (phenolation), and caustic (alkali treatment). Both the UM and the chemically modified lignin were introduced into plywood glues by direct addition and by reaction with phenol and formaldehyde to synthesize lignin-PF resins. The performance of lignin in the glues was assessed by making plywood from Douglas fir, poplar, or white spruce veneer and using CSA plywood standard test procedures. The key measure is the percentage wood failure, which is the relative integrity of the wood and the glue bond.

UM lignin successfully substituted for 20% of the PF resin; the glue performance was identical to that of a commercial plywood glue. However, at 50% PF resin substitution, there was a drop in the performance of the glue. Glues containing UM lignin, reacted with phenol and formaldehyde to synthesize a UM-PF resin, also

performed poorly at 50% substitution.

Hydroxymethylation and phenolation of the lignin required extensive development of chemical protocols. The maximum phenol uptake onto Iogen Steam-Exploded Lignin was 42%, which is the highest percentage reported for any lignin. It was also higher than the uptake onto several commercial lignins. The phenolated lignin showed a markedly improved formaldehyde uptake. Monitoring the extent of the hydroxymethylation reaction proved difficult because of interference of the lignin with the assays and the variety of reaction byproducts. Nonetheless, hydroxymethylated and phenolated lignin were both physically acceptable for direct addition to plywood glue or to synthesize resin with phenol and formaldehyde.

Of the chemically modified lignins, hydroxymethylated lignin-PF resin performed the best. This lignin showed a wood failure of about 70% at 50% substitution, which is only marginally less than the CSA standard of 80% wood failure, and is the best reported for lignin substitution into PF resin. Mild (70°C) alkali treated lignin performed almost as well, with a 60% wood failure. In spite of the high phenol uptake, none of the phenolated lignin glues averaged over 50% wood failure at 50% substitution. The best performance (50% wood failure) was from a phenolated lignin-PF resin; the direct addition of phenolated lignin to plywood glue resulted in 35% wood failure.

RÉSUMÉ

Il s'agit du rapport final sur "l'utilisation de la lignine obtenue par explosion à la vapeur dans les adhésifs pour contreplaqué", préparé par la société Iogen. La lignine faisant l'objet du présent travail est le sous-produit de la transformation du bois en éthanol; elle est obtenue à partir de bois soumis à un traitement rapide à la vapeur (explosion à la vapeur), puis digéré sous l'action d'enzymes (cellulase). Cette lignine a été utilisée pour remplacer la résine de phénol-formaldéhyde (PF), principal constituant des préparations de colle pour contreplaqué.

La lignine a été testée sous une forme non modifiée (NM) et après avoir réagi chimiquement avec du formaldéhyde (hydroxyméthylation), du phénol (phénolation) et du caustique (traitement alcalin). La lignine NM et la lignine chimiquement modifiée ont été incorporées dans des colles pour contreplaqué par addition directe et par réaction avec du phénol et du formaldéhyde, ce qui a donné des résines de lignine-PF. On a évalué la performance de la lignine dans les colles en soumettant des panneaux de contreplaqué fabriqués à partir de plaques de pin Douglas, de peuplier ou d'épinette blanche, à des essais standard de l'ACNOR sur les contreplaqués. La mesure la plus importante est le pourcentage de rupture dans le bois, qui représente l'intégrité relative du lien entre le bois et la colle.

Lorsque l'on remplaçait 20 % de la résine de PF par de la lignine NM, la performance de la colle obtenue était identique à celle de la colle commerciale pour contreplaqué. Cependant, lorsque l'on remplaçait 50 % de la résine de PF par de la lignine, la performance de la colle diminuait. Les colles renfermant de la lignine NM ayant réagi avec du phénol et du formaldéhyde pour donner une résine de lignine NM-PF n'ont pas non plus donné de bons résultats lorsque le taux de remplacement était de 50 %.

L'hydroxyméthylation et la phénolation de la lignine ont nécessité l'élaboration de protocoles chimiques détaillés. La proportion maximale de phénol absorbé dans le cas de la lignine obtenue par explosion à la vapeur suivant la méthode de la société Iogen s'élevait à 42 %, soit le pourcentage le plus élevé signalé pour une lignine. Elle était également plus élevée comparativement à plusieurs lignines commerciales. Dans le cas de la lignine phénolée, l'absorption de formaldéhyde était nettement supérieure. Il s'est avéré difficile de contrôler l'étendue de la réaction d'hydroxyméthylation à cause de perturbations dues à la lignine lors des essais et à cause de la diversité des sous-produits réactionnels. Néanmoins, il était physiquement possible d'incorporer directement la lignine hydroxyméthylée et la lignine phénolée à la colle pour contreplaqué ou de l'utiliser pour synthétiser de la résine avec du phénol et du formaldéhyde.

Parmi toutes les lignines chimiquement modifiées, c'est la résine de lignine hydroxyméthylée-PF qui donnait les meilleurs résultats. Le pourcentage de rupture dans le bois de cette lignine s'élevait à 70 % lorsque la moitié du PF était remplacé, ce qui n'est que légèrement inférieur à la norme de l'ACNOR (80 % pour la rupture dans le bois). Il s'agit du meilleur taux obtenu en remplaçant une partie de la résine de PF par de la lignine. On a obtenu des résultats presque aussi bons, soit un taux de 60 %, avec la lignine soumise à un doux traitement alcalin (70 °C). Malgré la forte proportion de phénol absorbé, avec aucune des colles de lignine phénolée la rupture dans le bois ne dépassait 50 % pour un taux de remplacement de 50 %. Dans ce cas, la meilleure performance (50 % de rupture dans le bois) a été obtenue avec une résine de lignine phénolée-PF; l'incorporation directe de lignine phénolée à la colle pour contreplaqué a donné un taux de rupture dans le bois de 35 %.

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1.0 INTRODUCTION

Lignin is one of the most abundant natural products on earth. It is a major component of many plants with a content ranging from 3% in corn stalks to 33% in softwoods. Any large-scale biomass conversion industry necessitates a market for the lignin, both to increase the total product revenues and to avert a waste disposal problem. One option is to burn the lignin on site to produce energy. This process, which is carried out on most of the lignin from the pulp and paper industry, results in a very low value from the lignin. It is much more desirable to make high value products from the lignin.

Lignins are used for the production of a wide range of specialty chemicals and materials (review by Chum, et.al, 1986). Some of their industrial surfactant applications include drilling muds, animal feed binders, gypsum board and construction materials, concrete and cement admixtures, and dust control and soil stabilization agents. Other markets for lignin include rubber reinforcement agents, asphalt extenders, and as a precursor in vanillin production. Although many of these markets are large, it is clear that new applications must be developed to absorb the huge quantities of lignin that will be produced in biomass-based processes.

Lignin-based adhesives are among the most widely studied

potential applications of lignin. In particular, one of lignin's large proposed uses is as a major constituent in phenol formaldehyde (PF) thermosetting resins. These resins are used primarily for plywood (500 million pounds in 1983) and also for particle board, foundry binders, laminates, and in the production of insulating materials. In these products, phenol is condensed with formaldehyde to form a stiff resin matrix. Lignin's similarity in chemical structure to a PF resin condensate suggests that it could be an effective substitute for PF resin. Figure 1-1 shows phenol along with the three building blocks of lignin: P-hydroxyphenol, syringaldehyde, and guaiacol. In a phenol formaldehyde resin, formaldehyde is used to form methylene links between phenols to produce a rigid matrix (Figure 1-1B). In lignin, the three building blocks can be condensed with one another by adding formaldehyde to form methylene links. The lignin can also be condensed with phenol by using formaldehyde as a coreactant. This report focuses on the substitution of PF resin by lignin in plywood adhesives.

1.1 Plywood Manufacturing and Testing

Plywood is generally made by binding hardwood or softwood veneer with a liquid glue. The veneer is pretreated by drying it to the acceptable moisture level of 1-4%. The glue consists of resin, of which PF resin is common, along with powdered fillers, extenders, catalysts, and water, which are combined on site by

plywood mills. A typical glue formulation is shown in Figure 1-2. Water accounts for more than 50% of the total weight of glue. The resin is the major constituent and primary adhesive network former. The catalyst, of which soda ash is typical, is added to hasten the resin curing reaction. Fillers, extenders and water are added to adjust the viscosity of the glue to the proper value for spreading (about 2200 centipoise), modify penetration into the wood, and reduce the cost of the glue. The glue is then spread onto the plywood, and the boards pressed at cold (ambient) and then at hot (150°C) conditions. The boards are stacked for 24 hours after pressing to cool down and cure and then are ready for sale or for performance testing.

Plywood performance testing follows Canadian Standards Association (CSA) procedures. Samples of 1 inch by 4 1/2 inches are tested for shear strength and percentage wood failure, which is the proportion of the bonded wood that breaks before the glue line breaks. The shear strength and wood failure are tested under three conditions: dry, after submergence in boiling water (boil test), and after vacuum and high pressure conditions (vacuum/pressure test). Typically, 32 samples are run on each test because there is often a broad distribution in performance. The CSA specifications are quite detailed, but in general the average of all specimens in each test must be at least 80% wood failure.

1.2 Lignin in Plywood Glues

Figure 1-3 shows three steps in the plywood glue process in which lignin, with or without chemical modification, can substitute for PF resin:

A. Direct addition to the glue mixture;

B. Reaction with PF resin;

C. Reaction during resin synthesis.

In all cases, the amount of other glue ingredients added, especially water, is modified when lignin is present to produce a glue of the desired viscosity.

The lignin used in this study was Iogen Steam-Exploded Lignin. Iogen Steam-Exploded Lignin is made by cooking poplar wood with steam, followed by rapid decompression ("explosion"). The exploded wood is hydrolysed with cellulase enzymes to convert at least 85% of the cellulosic fraction to soluble sugars. The hydrolysis residue is washed with water and then dried to form a homogeneous, caustic soluble, water insoluble powder with a methoxyl content of at least 15% (Foody, et.al., 1979). Steam-Exploded Lignin has a narrow and relatively low molecular weight distribution, which should enable it to be incorporated into phenol formaldehyde structures. Preliminary tests have shown Steam-Exploded Lignin to be more reactive than commercial lignins (Glasser, 1983), whose low reactivities lead to uneconomically

long cure times. The high reactivity of Steam-Exploded Lignin allows it to directly replace PF resin, the most expensive component of the glue, instead of merely acting as an inert filler (Foody and McGuire, 1986). Furthermore, Steam-Exploded Lignin can be added to glues in a powdered form at the plywood plant, causing minimal change in the practice of mixing glues.

Preliminary testing bears out some positive results of Steam-Exploded Lignin relative to pulp and paper lignins for use in plywood adhesives, as shown in Figure 1-4 (Foody and McGuire, 1986). Different lignins were tested at various phenol substitution levels in plywood resins. Lignosol DXD, a lignosulphonate, decreased the strength of the glue even at low levels of addition. Westvaco's Indulin-AT, a purified Kraft lignin, was able to sustain performance out to 25% substitution for phenol, and decreased the strength above that. Iogen's Steam-Exploded Lignin maintained performance out to 50% substitution, suggesting that its unique properties allow it to work better in PF resin systems than commercially available lignins. However, this preliminary testing was not carried out with commercial conditions or glue formulations.

The successful performance of Steam-Exploded Lignin in large scale testing was demonstrated in 1987 at a commercial plywood mill (Anonymous, 1987). The glue containing lignin at 30% substitution for PF resin performed as well as the commercial

glue.

Although Steam-Exploded Lignin has shown several positive indications over commercial lignins for use in plywood adhesives, there is little information available on the practical use of Steam-Exploded Lignin. The mechanism of glue formation is not well understood. The effect of chemical modifications of the lignin on performance in plywood adhesives has not been reported. The upper limit of substitution of PF resin has not been characterized. The lignin has been tested only by direct addition into the glue and not by inclusion in resin synthesis.

1.3 Objective and Approach

The objective of this project was to develop and test Steam-Exploded Lignin formulations and chemical modifications in plywood adhesives. Unmodified and chemically modified lignin was introduced into the glues by: A) Direct substitution for PF resin, B) Reaction with PF resin prior to glue mixing, and C) Reaction with phenol and formaldehyde during resin synthesis. The chemical modifications to the lignin included reactions with formaldehyde (hydroxymethylation), phenol (phenolation), and sodium hydroxide (alkali treatment). All plywood containing lignin glues was made and tested according to CSA procedures.

2.0 UNMODIFIED (UM) LIGNIN

Section 2.1 describes the direct substitution of unmodified (UM) lignin for PF resin at various levels on three types of veneer. Section 2.2 describes the co-reaction of lignin with commercial PF resin, while Section 2.3 describes UM lignin added during PF resin synthesis. A detailed description of the materials and methods is found in Appendix 6.1.

2.1 DIRECT SUBSTITUTION

Lignin Addition Procedures

Figure 2-1 shows the processing steps used to prepare plywood, from the veneer's arrival through its testing. Douglas fir (from Crestbrook, Inc.), poplar (from Normick Perron, Inc.), and white spruce (from Zeidler, Inc.) were the three veneers tested. All veneer was glued and pressed in two stacks of three boards. Each plywood mill supplied the glue formulation normally used for the respective commercial processes. The performance of these control glues was compared with lignin glues, which contained Iogen Steam-Exploded Lignin at up to 70% substitution of PF resin. Compositions of all the glue formulations used on Douglas fir are shown in Figure 2-2, poplar in Figure 2-3 and spruce in Figure 2-4. The glues were spread at a loading of 60 to 70 pounds per thousand square feet of double glue line (lb/MDGL).

PF resin, lignin, and water account for over 85% of the glues. The glue mix is adjusted to a viscosity of 2200 cp by adding water. The water content increases with increasing lignin loading, from 55% moisture in a commercial glue to 67% moisture at 70% PF substitution. The plywood made from each glue was tested using dry, boil, and vacuum/pressure test procedures. The performance of the plywood with glue lignin was also characterized by isolating the glue line with paper.

UM Lignin Performance

Douglas fir veneer wood failure results are shown in Figures 2-5 through 2-7 for dry, boil, and vacuum/pressure tests, respectively. In each test, increasing substitution of PF by lignin reduced the performance of the glue. At 20% substitution, the lignin glue performed nearly as well as the control glue. However, at 50 and 70% substitution, glue performance dropped off significantly. The strength results, Figures 2-8 to 2-10, correlated with the wood failure results, i.e. increasing substitutions resulted in decreasing strengths, as well as decreasing wood failures. Two trends of the wood failure and strength tests are usually observed. The vacuum/pressure test is the most severe and results in the lowest wood failure, and the strength tests usually correlate with the wood failure. Therefore, most of the data to be shown in the following sections will be the wood failure results from the vacuum/pressure test.

Poplar wood failure results are shown in Figure 2-11 for the vacuum/pressure test. As with Douglas fir, increasing PF substitution decreased the wood failure. However, the effects of PF resin substitution were more pronounced at the lower substitution levels. Unlike the minor decrease with the Douglas fir, 20% substitution of PF resin on poplar significantly decreased the performance relative to the control. The strength results for poplar are shown in Figure 2-12. Increasing PF substitution resulted in decreasing strength. This result contrasts with that at the Temfor Mill trial (Anonymous, 1987), in which the glue containing lignin at 30% substitution for PF resin performed as well as the commercial glue. The reason for this discrepancy in results is not clear.

The white spruce wood failure results (Figure 2-13) indicated that the lignin glue (21% substitution) equalled the performance of the commercial glue. However, both glues performed below CSA standards. The strength results for white spruce (Figure 2-14) showed that the commercial glue results were slightly higher than those of the lignin glue. While lignin based glues appear to be suitable on spruce veneers at the 21% level, neither the commercial glue nor the 21% substituted glue performed adequately on spruce. The reason for the poor performance of the control is not clear. It may relate, for example, to poor quality spruce veneer sent from the mill. As a result of this uncertainty, no further work with spruce veneer was carried out.

The reason for the decreasing performance of the lignin glues with increased substitution likely relates to the glue formulations. By increasing the amount of lignin in the system, the demand for water to maintain the target viscosity increased dramatically, as shown in Figures 2-2 to 2-4. The glue solids are decreased by 18% to make a 70% substitution glue. The effect of the additional water is likely detrimental to glue performance, because of the decrease in glue solids.

A further effort was made to understand the nature of the lignin/PF system by isolating the glue line from the plywood system and testing it independently. The approach was to spread commercial and lignin glues onto several layers of paper towels. The paper is subsequently treated under the precise plywood mill curing conditions. By spreading the glues onto paper, the glue line can be removed and studied independently of the wood. It was hoped that such an approach could be used as an accurate screen for glue systems and would have a higher degree of repeatability and require fewer assays than a full CSA plywood test.

The test system is shown in Figure 2-15. Several sheets of paper were on each side of the glue line. The glued paper was bound by single sheets of veneer, which were in turn bound by a sheet of aluminum foil and finally by 3-ply boards. The entire assembly was pressed both cold and hot at plywood-pressing conditions.

The proximity of the paper to the veneer permitted moisture in the glue to escape into the veneer, as in actual plywood pressing. Foil was used to limit moisture escape to that which might be observed under mill conditions. For example, a piece of foil was placed at the points of "symmetry" through which moisture flux would be expected to be zero.

Of several papers tested for their suitability in this procedure, paper towels were found to be the best. Spreading was too difficult on tissue paper, and writing paper was practically impenetrable to the glue and moisture during the cure. Seven layers of papers on either side of the glue line were found to be optimal because glue was prevented from penetrating into the veneer while the paper did not add appreciable thickness to the plywood stack when pressed.

The degree of moisture removal from the glue line was quantified for glues with up to 52% PF substitution. A histogram of each glue formula is shown in Figure 2-16. At the commercial hot press (cure) time of 5 minutes, less than 55% of the moisture was removed in all the glues (Figure 2-17). By 12 minutes, approximately 90% of the moisture had been removed. The percentage of moisture removed was fairly independent of the PF substitution or initial moisture content of the glue. From this result, it follows that the solids content of the glues at any time during the cure depends directly on the initial solids

content, and this is shown in Figure 2-18. The glues initially had different solids contents; subsequently, all of the glues had similar rates of increase of solids content with time. This observation confirms the suspicion that a high water content in the initial glue will cause a high water content after curing. One would expect this to weaken the integrity of the glue bond.

The effects on the curing process of the high moisture contents in lignin glues were observed by contacting the paper glue lines with dilute caustic at 50°C. The solubility of lignin in caustic decreases with increasing molecular weight. Therefore, one expects that as the glue cures, the amount of soluble components will decrease. The presence of lignin did not appear to alter the fraction or rate of formation of insoluble products (data not shown). However, there may be many interfering compounds on the UV spectrophotometric assays that were performed, so the results of this test are probably not definitive.

Another measure of the cure kinetics is that the shear strength of the paper glue lines is expected to increase as the glue cures. The results of this testing are shown in Figure 2-19. Increasing press time resulted in increasing strengths. Generally, the higher the press time, the more distinguishable the glues, with the strongest glues having the lowest degree of substitution. This is in agreement with the board test results with increasing lignin substitution. However, further work is

required for this to be an accurate, reproducible assay. The paper shear strength routinely varied by 40% for a given glue formulation tested on paper. The variation was caused by non-uniformity of the glue line, which was in turn caused by the roughness of the wood surface, the difficulty in spreading the glue evenly on paper, and probably moisture gradients in the glue line (edges dry more rapidly). All of these problems are probably surmountable. The paper test, and especially the strength test, show promise in providing more information about the glue line.

Direct addition of lignin does not appear to be a suitable means to achieve a high PF substitution. Lignin cannot directly substitute for PF resin without deleterious effects on glue performance at levels of 50%. When unmodified lignin is simply added to a precured resin, it is possible that the system suffers from a shortage of cross-linking units. This means that lignin's role as an integral part of the glue network would be reduced. The following sections focus on the reaction of UM lignin with PF resin to overcome these problems.

2.2 UM LIGNIN CO-REACTION

Introduction

There are several stages of the plywood glue manufacturing

process at which lignin could conceivably be added (Figure 1-3). One option is that lignin could be coreacted with a commercial resin in the presence of a third, binding compound. This section will describe the coreaction of unmodified lignin with a commercial PF resin in the presence of formaldehyde. The rationale for the use of formaldehyde is that it might coat the lignin molecules, as with phenol, making a composite receptive to PF resin polymerization.

Lignin PF Co-reaction

A lignin-PF mixture was made having, on a solids basis, 33% lignin, 6.6% formaldehyde, and 50% PF resin solids; the balance was NaOH to adjust the pH to 13.3. The formaldehyde loading on lignin was 20% (at an average lignin monomeric molecular weight of 170, the nominal molar ratio was about 1:1) to ensure sufficient cross-linking capacity. The solids concentration, 37%, was the maximum that maintained a "reasonable" viscosity before reaction (less than about 6000 cp). Commercial PF resins are about 44% solids.

The lignin-PF mixture was heated at 70°C to polymerize. Figure 2-20 shows the viscosity versus time profile for the lignin-PF mixture. The initial viscosity was 340 cp which dropped to 161 cp within 2 hours, then increased to 382 cp after 7.5 hours and to 468 cp upon sitting overnight. The initial drop in viscosity

was highly reproducible and may be related to the fate of formaldehyde in the system. No free formaldehyde was present at 2 hours. The drop in viscosity may have been the result of the degradation of formaldehyde not ultimately used as linkage units between lignin and phenol. This degradation would occur via the Cannizzaro reaction in which formaldehyde is converted to formic acid and methanol under high pH and warm temperatures (March, 1977). The subsequent increase in viscosity is believed to indicate that polymerization occurred as: a) the lignin reacted with formaldehyde and crosslinked; and b) the PF resin self-condensed.

Co-reacted Lignin Plywood Glue

The lignin-PF resin performance in a softwood plywood glue was compared with the commercial PF resin used to produce it. The glues were formulated to have the same concentration of resin solids plus lignin, 31%. The lignin substituted for 34% of the PF solids. Figure 2-21 shows the glue compositions. The glue formula is described in detail in Section 6.1.2.

The glue was used to make Douglas fir plywood. The wood failure results (Figure 2-22) indicated that none of the lignin/PF coreacted resin glues averaged over 37%. The commercial glue results, although significantly higher in all three tests, did not meet CSA specifications. The data displayed unusually large

ranges. The strength results (Figure 2-23) indicated that the commercial glue displayed higher strength in all three tests. The coreacted resin glue showed very low strength, particularly in the boil and vacuum/pressure tests.

One plausible explanation for the poor performance of the lignin glues is that the lignin may not have condensed with the formaldehyde and PF resin; the lignin may have been totally inert, or the lignin may have only self-condensed with methylene linkages from the formaldehyde. In such cases, the number of lignin/phenol binding sites would not have increased as a result of the 70°C heating. The lower performance of the coreacted resin may have been related to, in part, a higher water content in the glue. There was approximately 12% (4 lbs/MDGL) more water in the coreacted glue. However, the increase in water content in the glues with coreacted lignin was comparable to that of direct substitution glues (19% at 21% substitution), which had much better performance (65% wood failure in vacuum/pressure testing).

2.3 UM Resin Synthesis

Introduction

In a typical PF resin synthesis, water is split off in the reaction of phenol and formaldehyde in what is known as a resol condensation reaction (Figure 1-1B). The ratio of formaldehyde

to phenol as well as the temperature, reaction time, pH, and catalyst influence the extent to which the condensation takes place. Under alkali conditions, the formation of methylene linkages that join phenol and formaldehyde occurs rapidly (Sellers, 1985). The product is a very reactive matrix-like structure. In a plywood glue, the hot-pressing process accelerates the condensation reaction, although resol resins continue to polymerize even at low temperatures. Desired physical properties of the resin include a high heat distortion temperature, high modulus, high tensile strength, low flammability and good moisture resistance (Sellers, 1985). Generally, strength and moisture resistance increase with an increasing ratio of formaldehyde to phenol (F/P). Resin flowability, however, decreases. Excessive moisture migration away from the glue line results in a crusty, crumbly resin. Poor adhesive wood bonds result.

Given the structural similarity between lignin and phenol, it is plausible that lignin can undergo resol condensation with phenol in the presence of formaldehyde. Presumably, increased crosslinking of lignin with phenol and formaldehyde would increase the extent to which lignin is incorporated into the plywood adhesive network. This section describes the synthesis of a lignin-PF resin and its use in plywood adhesives at 50% substitution for the phenol.

UM Lignin - PF Resin Synthesis

A typical viscosity and temperature profile over time during commercial PF resin synthesis is shown in Figure 2-24 (Muller, et.al., 1984). Typically, a 44% solution of phenol and formaldehyde is used in molar ratio 1:2. Heating at 85°C causes a rapid increase of the viscosity up to a maximum range of 32,000 to 48,000 cp. This is indicative of the crosslinking reaction. At this point, caustic is added, reducing the viscosity to approximately 200 cp. The temperature is also lowered to 70°C. Rapid increase of the viscosity occurs again up to a maximum tolerable range of 12,000 to 16,000 cp. A final caustic addition at this point lowers the viscosity to 1000 cp. The resin is rapidly cooled to 25°C, thereby stabilizing the viscosity for long periods. Total time of the reaction is just under 3 hours.

The above generalized scheme was modified to emulate the synthesis of a specific commercial PF resin, Borden BCW-2001, as a first step before attempting the synthesis of a lignin-PF resin. The temperature was decreased to 80°C during critical periods of the reaction, which slowed the rapid increase in viscosity, making it more manageable. The viscosity levels at which sodium hydroxide was added were also lowered from over 10,000 cp to 1000 cp, again to decrease variability and increase the ease of control.

A PF resin was prepared with a viscosity of 340 cp, which is close to that of BCW-2001 of 400-600 cp. The viscosity and temperature profile of the reaction is shown in Figure 2-25. The system ran at much lower viscosity levels than that of Muller, et.al. In addition, the Iogen resin synthesis reaction took almost twice the time reported by Muller, et.al. However, the same time period of 3 hours was required for Muller, et.al., and Iogen after 100 cp was reached.

The Iogen PF resin was tested in Douglas fir plywood and compared to the Borden resin. The wood failure results (Figure 2-26) indicated that Iogen PF resin performed similarly to the commercial glue in the dry and boil tests. The Iogen resin vacuum/pressure results were slightly lower with an extremely wide scatter in the data. The strength results (Figure 2-27) indicated slightly higher strength for Borden glue in the boil test. The dry and vacuum/pressure results were the same. Although the performance of the commercial resin was slightly better than the Iogen PF, neither glue's wood failure results met CSA specifications in any of the three tests. We therefore conclude that within the limitations of test procedure, the Iogen resin-making procedures give comparable results to the commercial resin.

A 44% solids aqueous solution of formaldehyde, phenol, lignin, and caustic was reacted to synthesize a UM lignin - PF resin.

The reaction mixture consisted of a 2:1 molar ratio of formaldehyde to phenol plus lignin monomeric units, at an average lignin monomeric molecular weight of 170 (Foody, 1985). The UM lignin substituted for 50% of the phenol in the commercial resin. The viscosity profile of the lignin-PF resin synthesis is given in Figure 2-28. The final viscosity of this resin was 450 cp. The synthesis differed from the PF resin synthesis in two significant respects. Firstly, the run took only 3.8 hours for completion compared to 6 hours for the PF resin. Secondly, the first viscosity peak was significantly higher and the second peak lower than 1000 cp. The second viscosity peak must be lower than 1000 cp to assure that the final viscosity is within the target range of 400-500 cp. The additions of caustic diluted the final product to 40% solids.

The solids content of the UM lignin-PF resin of 40% was between the 39% solids for Iogen PF resin and 44% for the commercial resin. Unlike the lignin-free resins, the UM lignin-PF resin had a measurable amount (1.5%) free formaldehyde, which indicates that about 85% of the formaldehyde reacted. The UM lignin PF resin was smooth and homogeneous, and thus judged suitable for use in a plywood glue.

Testing of UM Lignin-PF Resin Glue in Plywood

A plywood glue was prepared with the lignin PF resin with the

same resin solids plus lignin concentration as the commercial glue and the Iogen PF glue. The lignin substituted for 31% of the resin solids in this glue. The composition of each glue is shown in Figure 2-29. Although the resin solids plus lignin concentrations were the same, the filler and extender solids ingredients were reduced by 40% for both the UM lignin-PF and Iogen PF glues relative to the commercial glue to maintain the 2200 cp glue viscosities. At this low filler concentration, the UM lignin resin glue required the same amount of water as the Iogen PF resin glue.

The wood failure results of the three glues on Douglas fir plywood are shown in Figure 2-30. The UM lignin resin glue averaged between 32 and 46% wood failure for the three tests. Iogen PF resin glue averaged between 52 and 68%. The commercial glue averaged above 80% for all three tests and passed CSA specifications. The strength results are given in Figure 2-31. The commercial glue and Iogen PF resin glue showed approximately the same strength. The lignin resin glue showed lower strengths in the dry and boil test and similar strength in the vacuum/pressure test to the other two glues.

The board tests results indicate that substituting lignin for 50% of the phenol in a resin formulation lowers the performance of the glue. This does not rule out the possibility of using unmodified lignin in resin synthesis at a lower substitution.

However, unmodified lignin might not be reactive enough to contribute significantly in the crosslinking which normally occurs when the glue is subjected to a hot press. The low strengths indicate that the resin is not bonding to the veneer, a likely consequence of lower reactivity.

The introduction of UM lignin into plywood glues by: A) direct addition, B) coreaction with PF resin, and C) reaction with phenol and formaldehyde in resin synthesis, resulted in suitable plywood glues at PF substitution levels of 20%, but not 50%. It appears that chemically modifying the lignin to make it more reactive is required for improved performance. The following sections will describe chemical modifications of Steam-Exploded Lignin.

3.0 CHEMICAL MODIFICATIONS TO STEAM-EXPLODED LIGNIN

This section describes the addition of formaldehyde (hydroxymethylation) and phenol (phenolation) to Steam-Exploded Lignin.

3.1 Hydroxymethylation

Introduction

This section describes the reaction of Steam-Exploded Lignin with formaldehyde. The reaction of formaldehyde and phenol is the

first step in the preparation of PF resin (Pizzi, 1983). This condensation reaction results in the formation of methylene bridges joining adjacent phenol groups (Figure 1-1B). The mode of action for this reaction is ortho- and para-directing. Thus, with phenol there are three places at which formaldehyde may bind. The result is up to five hydroxymethyl phenols in varying proportions, determined by the reaction conditions (Figure 3-1) (Forss, 1979). Condensing of the hydroxymethylol groups results in the formation of the methylene bridges.

Chemical modifications to lignin have been widely studied and shown to improve lignin performance in various applications (Sarkanen, et.al., 1971). Lignin, which is composed of an aromatic ring and a propylene side chain, is a good candidate for the condensation reaction with formaldehyde. However, the presence of methoxyl groups limits the degree to which the reaction can occur.

Two types of reactions of lignin and formaldehyde are possible (Young, 1985). The first is a Lederer-Manasso type reaction in which the formaldehyde is directed towards unoccupied ortho positions of the ring. Steam-Exploded Lignin is comprised of 47% syringl, 28% guaicyl, and 25% P-hydroxy type lignin (Foody, 1985). Therefore, reactions at the ortho position are likely to occur. The second reaction is a Tollen's type reaction involving a mixed aldol condensation at the alpha carbon of an activated

proponyl side chain. Formaldehyde binds this alpha carbon resulting in a hydroxymethylol group. These two reactions result in an activated lignin which can then bind with phenol and presumably be more suitable for bonding with plywood. Figure 3-2 illustrates these two reactions.

Investigations of lignin hydroxymethylation have focused on lignosulfonate, although some results with Steam-Exploded Lignin have been reported. Typically, the reactions are carried out in excess formaldehyde at a pH of between 11 and 12 and at temperatures of 20 to 100°C (Clarke and Dolenko, 1978, Lin, 1980, Dilling, 1985). Lin and Detroit (1981) found that the rate of reaction between lignin and formaldehyde is directly proportional to the phenolic hydroxyl content of the lignin. The rate of hydroxymethylation of lignin is also influenced by pH, temperature, and aeration. Based on the structure of Iogen's Steam-Exploded Lignin, it is estimated that 5-7% formaldehyde by weight would be the maximum uptake level possible (Foody, 1985). This corresponds to the uptake measured by Muller and Glasser.

Various methods have been used to quantify the level of hydroxymethylation. Muller and Glasser (1984) used H-NMR analysis. The change in hydroxyl content of lignin after reaction is a quantitative measure of formaldehyde uptake. The conclusion of this work was that formaldehyde does react with Steam-Exploded Lignin, predominantly at the side chain rather

than at the aromatic ring. Although the work of Muller and Glasser represented a major step forward in understanding the reaction of formaldehyde and lignin, the H-NMR technique is not suitable for routine assessment of the reaction. Infrared spectroscopy, which is much simpler than H-NMR, is incapable of distinguishing between unreacted and hydroxymethylated lignin (Sutcliffe, 1987).

This section describes the uptake of formaldehyde onto Steam-Exploded Lignin at various pH (10.5 and 11.5) temperature (70°C and 85°C), aeration, and formaldehyde levels. In all cases the hydroxymethylation reactions were carried out in the presence of a pH buffer to ensure a constant reaction environment over time. The lignin concentration was dilute (less than 1%) to minimize product-mediated effects. Two methods were used for measuring formaldehyde uptake. A direct method involved measuring the weight gain of the lignin after formaldehyde addition. The second method was an indirect method in which the formaldehyde uptake was inferred from the measurements of unreacted formaldehyde and reaction by-products, namely formic acid, which is produced during the breakdown of formaldehyde by the Canizzaro reaction (March, 1977). Further details on the procedures are found in Appendix 6.2.

Results and Discussion

The accurate measure of formaldehyde uptake onto lignin was not possible by either of the methods used. In general, no free formaldehyde was present in solution after the reaction, which indicates that all of the formaldehyde either condensed with the lignin or was converted to other products. A slight reduction in the weight of the lignin was observed after 24 hours of reaction (Figure 3-3). This may indicate that an increase in acid soluble lignin during the reaction offset any gain in weight of insolubles due to condensation of the formaldehyde with lignin.

Unrealistically high levels of formaldehyde uptake were measured by inference from formaldehyde disappearance and formic acid formation. Figure 3-4 shows a maximum of 76% formaldehyde uptake on lignin. This amount is about ten times greater than reported (Muller and Glasser, 1984) and corresponds to as much as 3.9 formaldehyde molecules per lignin C9 unit. Up to 90% formaldehyde can be taken up onto pure phenol, or 3 formaldehyde molecules per phenol. Therefore the results indicate a formaldehyde uptake level onto lignin which is theoretically impossible. It can only be assumed that formaldehyde is being converted into a by-product other than formic acid. Perhaps large amounts of methanol are produced.

3.2 Phenolation

The reaction of phenol with lignin before the subsequent

crosslinking reaction with formaldehyde is the subject of this section. It is hypothesized that derivatizing the lignin with phenol makes the lignin more reactive. This increases the amount of formaldehyde that reacts with the lignin during resin synthesis, and thereby improves the performance of the resin.

There is considerable information available on the phenolation of spent liquor from sulfite pulping, which has been reviewed by Foster (1979). In general, lignin or lignosulfonate are reacted with phenol under highly acidic conditions (pH 2-4). Foster's preferred temperature range is 135°C-250°C with reaction time of 2-4 hr. The reaction has conventionally been run at these conditions for two reasons:

1. The phenolation reaction is acid-catalyzed;
2. An excess of phenol and lack of water drive the reaction to the desired equilibrium.

There is sharp disagreement concerning the mechanism by which phenol reacts with lignin. Kratzl and Oburger (1980), who studied the reaction of phenol with small aromatic molecules, concluded that phenol combines with the alpha-aliphatic carbon (see Figure 3-5). The work of Kratzl and Oburger is consistent with the notion that phenol substitutes onto sulfonated carbon atoms. However, Foster observed that the amount of phenol uptake exceeded by twofold the amount of sulfonate groups liberated

during phenolation. An alternative reaction mechanism, proposed by Muller and Glasser (1984) is that phenol adds onto alpha-hydroxyl carbons on the aromatic ring which have methylol groups (formaldehyde added). This mechanism also fails to describe Foster's results, because he obtained a significant phenol uptake without pre-reacting the lignosulfonate with formaldehyde.

Reactivity of Phenolated Lignin with Formaldehyde

Phenolated lignin is highly reactive with formaldehyde. This suggests that the problems for a glue preparation caused by lignin's low reactivity and inability to become incorporated into a resin matrix can be ameliorated by "pre-reacting" lignin with phenol. The resulting co-polymer of lignin and phenol might be expected to condense effectively is a plywood glue system.

These results are illustrated in Figure 3-6 which compares the reactivity of formaldehyde with phenolated lignin, and the amount of phenol and lignin, respectively, present in the phenolated lignin co-polymer. Unreacted lignin showed very little formaldehyde uptake, while the phenolated lignin shows a formaldehyde uptake equal to roughly the sum of that of the phenol and lignin present. These results suggest that a low lignin reactivity is ameliorated by phenolation so that lignin can become covalently bonded into a structural resin condensate.

Phenolation of Commercial Lignins

Table 3-1 summarizes the phenol uptake onto lignin from several commercial sources. The procedures for working with the various types of lignin were similar, with only minor changes to the phenol assay.

Table 3-1 shows that, at standard test conditions, the phenol uptake onto Iogen Steam-Exploded Lignin was about twofold greater than that for the other lignins. This suggests that Steam-Exploded Lignin is more reactive toward phenol than were the other lignins. By choosing more severe conditions, Foster obtained a maximum phenol uptake of 36% onto Softwood Spent Sulphite liquor, which was similar to the maximum uptake of Steam-Exploded Lignin.

Table 3-1: Phenol Uptake onto Lignin

Lignin Source	Phenol Uptake (%) at Test Conditions	Maximum Measured Phenol Uptake (%)
Iogen lignin	33	42
Indulin AT	15	
Hardwood SSL	14	
Reed Lignosulfonate	13	
Softwood SSL	17	
	21[2]	36[2]*

* 220°C, 3 hr, anhydrous conditions, P/L = 2.5

[2] Foster (1979)

Note that the phenol uptake is high even in the absence of methylol groups. Therefore, the results in Table 3-1 are not consistent with reaction mechanism A (substitution onto aromatic carbons with formaldehyde attachments) shown in Figure 3-5. Because the results in Table 3-1 do not necessarily represent the maximum phenol uptake, the data cannot be interpreted conclusively in terms of the reaction mechanism B.

4.0 CHEMICALLY MODIFIED LIGNIN IN PLYWOOD GLUES

Chemically modified Steam-Exploded Lignin was used in plywood glues. The chemically modified lignins tested included hydroxymethylated (Section 4.1), phenolated (4.2) and alkali-treated (4.3). Detailed descriptions of the procedures are found in Appendix 6.3.

4.1 Hydroxymethylated Lignin

Several hydroxymethylated lignins were used in plywood glue formulation by "direct addition" and by reaction with phenol and formaldehyde in "resin synthesis".

4.1.1 Direct Addition of Hydroxymethylated Lignin

Hydroxymethylated lignin made at several conditions were used to make plywood glues. The lignin was added, as a powder, to a commercial glue formula in 50% substitution for phenol formaldehyde resin. The hydroxymethylation reaction conditions are listed in Table 4-1.

Figure 4-1 shows the composition of each of the lignin glues and that of a commercial glue. Most of the hydroxymethylated lignin glues required approximately 5 lb/MDGL lignin to achieve 50% resin substitution at target glue viscosity.

Table 4-1: Glue Preparations at 50% PF Substitution				
Glue Symbol	Hydroxymethylation Reaction Conditions			
	Added % CH_2O on Lignin	pH	Temp.	Atm.
F0	0	10.5	70	Nitrogen
F10	10	10.5	70	Nitrogen
F30	30	10.5	70	Nitrogen
T	30	10.5	85	Nitrogen
P	30	11.5	70	Nitrogen
A	30	10.5	70	Air
Commercial			None	
Lignin Control			None	

This is less than the 7 lb/MDGL required for UM lignin at 50% resin substitution. This difference was caused by the extremely large viscosity increasing effects of the hydroymethylated lignin. Figure 4-2 shows the effect on wood failure of increasing levels of formaldehyde addition. These hydroxymethylated lignins were prepared at 70°C, pH 10.5, under a nitrogen atmosphere with up to 30% formaldehyde on lignin initially present. There was about a 22% wood failure for lignin charged with 0% and 10% formaldehyde and the UM lignin. There was a slight increase in performance, to 31% wood failure, with the lignin charged with 30% formaldehyde. The commercial glue wood failure results of 73% were below CSA specifications, but significantly higher than the lignin glues.

The strength results for these glues (Figure 4-3) indicated the same trends as the wood failure results.

Figure 4-4 shows the effects of temperature, pH, and aeration on the performance of glues with hydroxymethylated lignin (30% formaldehyde charge on lignin). Starting from a "base case" of 70°C, pH 10.5, N_2 atmosphere reaction conditions, we see that increasing the temperature to 85°C or the pH to 11.5 are detrimental to glue performance. The wood failure dropped from 31% for the base case to 13% and 10%, respectively, at the higher temperature and pH. However, aeration during hydroxymethylation is beneficial to the glue performance. In this case, the wood failure increased from 31% to 38%, although this is still well below the commercial glue and CSA standards. The strength results for these glues (Figure 4-5) showed generally the same trends.

There are several plausible explanations for the poor performances of the hydroxymethylated glues. As with the UM lignin, the hydroxymethylated lignins sharply increased the water demand and thereby decreased the solids content of the glues. There was also difficulty in mixing these glues, which tended to have lumps caused by precipitates. Finally, although the formaldehyde uptake onto the lignin was not measurable in this work (Section 3.1), it has been shown that the expected maximum formaldehyde uptake onto Steam-Exploded Lignin is only 5-7% (Foody, 1985; Muller and Glasser, 1984). This level of formaldehyde uptake is probably insufficient to improve glue

performance significantly.

4.1.2 Hydroxymethylated Lignin PF Resin (HM-PF)

A PF resin with hydroxymethylated (HM) lignin substituting for 50% of the phenol was produced. The viscosity/temperature profile with time of this resin is shown in Figure 4-6 and follows similar trends as that for UM lignin in Figure 2-28. The temperature scheme of this resin was that 85°C was maintained until the predetermined viscosity of 1000 cp was reached, then 70°C until the end of the run. The run took 4.2 hours to complete, with completion defined as the point at which two viscosity peaks of 1000 cp had been reached. The duration of this run was about the same as that required for unmodified lignin resin after 100 cp was reached. Other characteristics of this resin included a final viscosity of 425 cp, a free formaldehyde content of 2.4% and a solids content of 42%.

When the HM lignin resin was used in a plywood glue, the results were encouraging. Figure 4-7 gives the wood failure results for all of the tests done with HM lignin PF resin. The 78% wood failure of the HM-lignin resin equalled that of the commercial control glue in the first test. However, in two subsequent tests the performance of the HM lignin resin dropped down to 62% wood

failure, while the commercial glue improved to 85%. For some reason, the UM lignin glues at 50% substitution performed extremely well in these tests, with average wood failures of 42% to 78%, which was much higher than the typical values of 30-50% (Section 2.1).

The strength results of HM lignin glue testing (Figure 4-8) show the commercial glue is 10-20% stronger than the HM-PF glue. However, the first test, which showed the highest HM-PF wood failure, also showed its lowest strength, so there is poor correlation between strength and performance in the HM-PF glues.

One reason for the relatively good performance of HM-PF glues is the similarity in composition to the commercial glue. As shown in Figure 4-9, the HM-PF resin glue had a solids content of 27 lbs/MDGL, which is very close to the commercial resin glue (28 lbs/MDGL). The UM lignin glue had only 20 lbs/MDGL solids. Addition of UM lignin results in a far greater demand for water than does HM-PF resin.

4.2 Phenolated Lignin

Phenolated lignin was used in plywood glues by direct addition and by reaction with phenol and formaldehyde in resin synthesis.

4.2.1 Direct Addition of Phenolated Lignin

The composition of plywood glue with phenolated lignin at about 45% PF resin substitution and a commercial glue are shown in Figure 4-10. Two fractions of phenolated lignin were used, based on solubility at pH 11. The caustic-soluble phenolated lignin glue requires 15% more water than the commercial glue. The caustic-insoluble lignin glue has the same moisture content as the commercial glue, which suggests that the insoluble lignin does not contribute substantially to the glue's viscosity.

The wood failure results for these glues are shown in Figure 4-11. Both phenolated lignin glues performed very poorly, with wood failures of 22% to 35%. The commercial glue far outperformed the lignin glues with an average wood failure of 78%. Surprisingly, the insoluble phenolated lignin glue was almost as strong as the commercial glue, which shows that the strengths did not correlate with performance (Figure 4-12).

The plywood glue results indicate that the direct addition of phenolated lignin is detrimental to the performance of a glue. It is possible that the increased reactivity of lignin with phenolation is not properly utilized without a binder of some sort to integrate the lignin with the rest of the glue ingredients, especially the resin.

4.2.2 Phenolated Lignin PF Resin

Resin Synthesis

The reaction conditions of a mixture of phenolated lignin, phenol, and formaldehyde was based on the HM lignin resin synthesis. As shown in Figure 4-13, the reactants were heated at 85°C until the viscosity reached 4000 cp, then caustic was added. The temperature was then reduced to 70°C, and the run continued until the viscosity reached approximately 400 cp. The second caustic aliquot was added and the resin was then cooled down. This run (Batch 1) took 4 hours and yielded a resin of viscosity 250 cp, which was increased to 510 cp with gentle 60°C heating. There was no free formaldehyde present in the resin, which was 36% solids, pH 13.2.

Another phenolated lignin resin (Batch 2) was prepared with the same reactants and no caustic addition. The reactants were mixed at 80°C until 425 cp viscosity was reached. This resin contained 1.3% free formaldehyde, 35% solids, and was at pH 11.53.

Phenolated Lignin Glue Preparation

There were four phenolated lignin resin glues prepared. These were from the Batch 1 and Batch 2 resins, as well as the Batch 2 resin adjusted to pH 13.2 with caustic (to match the pH of Batch 1) and to pH 12.9 (an intermediate value).

The composition of the glues prepared with phenolated lignin resin are shown in Figure 4-14. All glues had the same PF resin plus lignin as the commercial glue. This figure indicates that the glue with Batch 1 resin required slightly less water and more fillers than Batch 2 which has a lower pH. This suggests that the higher the pH, the lower the water requirements. In addition, when Batch 2 was adjusted to pH 13.2, the amount of fillers significantly increased and water decreased. In fact, this resin's composition was very similar to the commercial glue. The demand for water therefore depends on both pH and the processing used.

Additional glues were made with phenolated lignin from Batch 1, adjusted to pH 13.2, with 1% and 4% Tween. Tween is the trade name of a polysorbate surfactant that one might expect would increase the ability of the glue to penetrate into the wood. The composition of these additional phenolated lignin glues is shown in Figure 4-15. The addition of Tween increased the viscosity of the glues. To maintain 2200 cp viscosity fillers and resin were removed in equal proportions (water was not added). This reduced the resin content of the phenolated lignin resin glues from 31.6% to 29.1 and 25.0% for 1% and 4% Tween addition, respectively. The solids content of these two glues was 35% versus 45% for the commercial glue. In addition, a phenolated lignin glue was made by adjusting the viscosity by removing fillers and not adding

water. This glue had a total solids content of 38.7% and was comprised of 34.3% resin solids. Therefore, there was a 67% drop in filler ingredients with this phenolated lignin resin glue compared to the commercial glue.

Phenolated Lignin Glue in Plywood

The wood failure results of the phenolated lignin glues can be seen in Figures 4-16 and 4-17. Glue with Batch 1 resin had a 50% wood failure, which, although below CSA standards, was better than Batch 2 (35%) or UM lignin (30%). The Iogen PF and commercial glue surpassed CSA standards. The addition of Tween improved the performance of the Batch 1 glue only marginally for the 4% addition (wood failure = 43%) and not at all for the 1% addition. The best of the Batch 1 phenolated lignin resin glues was that glue having only fillers and no extra water, with wood failure results averaged 49%. Obviously the high resin content of this glue resulted in improved performance.

The strength results (Figures 4-18 and 4-19) indicated that the lignin glues were 20-40% weaker than the glues without lignin. The strongest lignin glues, Batch 1 and Batch 2 with no water added, also had the highest wood failure.

4.3 Alkali Treated Lignin

Introduction

Unforeseen results during the hydroxymethylation work suggested that alkali treated lignin performed better than hydroxymethylated lignin. This section describes a more detailed look at the alkali treatment of lignin, and its use in plywood glues.

UM Lignin was treated with sodium hydroxide (10% on lignin) at 70°C and 150°C, both with and without oxygen present. All treatments were for 6 hours. The four alkali treated lignins were characterized by methoxyl content (Figure 4-20). The results indicated that the aerated alkali treated lignin had a slightly lower methoxyl content than the N_2 purged lignins. The UM lignin control showed approximately the same methoxyl content as the oxygen-free treated lignins. Therefore, there was not significant degradation of the lignin during alkali treatment.

All alkali treated lignin glues at 50% PF resin substitution had the same composition, which was identical to that with UM lignin and required 25% more water than the commercial glue (Figure 4-21).

The wood failure results (Figure 4-22) indicated that the lignins treated at 70°C showed better performance than the unmodified lignins. The aerated 70°C treated lignin averaged 60% wood failure which was higher than the non-aerated lignin glue (42%

wood failure) and equal to an acid precipitated (purified) lignin glue. The 150°C alkali-treated lignin glues performed very poorly. Wood failure was under 20%. The commercial glues performed much higher than the other glues and met CSA standards.

The strength results (Figure 4-23) indicated that all the lignin glues showed approximately the same strength, about 40% less than the commercial glue.

It appears that alkali treated lignins show higher performance than unmodified lignins for low reaction temperatures. A temperature of 150°C appears to lead to reduced performance. Aerated treatment appears to be more favourable than non-aerated treatment, although the wide distribution in the wood failure for both 70°C treatments suggests that this difference may not be significant.

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Finally, we wish to acknowledge the support and encouragement of Douglas Hayes without whom this work would not have been possible.

6.0 APPENDIX

6.1 Unmodified Lignin

6.1.1 Direct Addition

Veneer: Douglas fir, 0.125" thick, was received from Crestbrook Inc. (Fort McCleod, Alta. and Golden, B.C.). Poplar veneer, 0.140" thick, was received from Normick Perron Inc. (Cochrane, Ont.). White spruce, 0.125" thick, was received from Zeidler Inc. (Edmonton, Alta.).

Upon receiving a shipment of veneer, it was cut into 11" x 11" sheets for making laboratory plywood specimens. The target moisture content was 1 to 4%. If required, the moisture content of the veneer was adjusted by drying at 50°C. The veneer was maintained at the target moisture content until the plywood was assembled.

Glue: Glue components consisted of: W-838 PF resin, supplied by Borden Chemicals (West Hill, Ont.), BCW-2001 PF resin, supplied by Borden Chemicals (Vancouver, B.C.), Cocob from Delyco, Inc. (Memphis, Tn), RX-100 from Aurun Mines (Surrey, B.C.), Cremo wheat flour from Maple Leaf Mills (Montreal, Que.), deionized water, and

Iogen lignin, Batch Number UM081AAC , that was precipitated in dilute sulfuric acid, of methoxyl content 16.65% (Iogen Corporation, Ottawa, Ontario).

Glue Preparation:

The glue was mixed using a low shear mixer. The amounts and types of fillers used in the commercial glues were specified by the plywood manufacturer who supplied the veneer. The glue was mixed by combining a portion of the resin and of the water together, then mixing in the powdered ingredients for 20 minutes. The remaining resin was then mixed in. Water was added in small increments until the proper viscosity was achieved. Glue viscosity was measured on a Brookfield RVT viscometer at a sample temperature of 25°C. The amount of water necessary to achieve the proper viscosity could not be determined a priori. However, water demand typically increased with increasing lignin levels. The glue formulations were designed to be as similar to the commercial formulation as possible, except where specified. Glue loading was described in terms of pounds per thousand square feet of double glue line (lbs/MDGL) the commercial unit of glue spread. The glue formulations for Douglas fir, poplar, and spruce in testing UM lignin are listed in Table 6-1.

Plywood Preparation

Figure 2-1 shows the processing steps used to prepare plywood, from the veneer's arrival through its testing. The plywood manufacturing conditions are listed in Table 6-2 for Douglas fir, poplar, and spruce.

Layup, Prepress, and Hot Press

The plywood was manufactured by rolling the glue on both sides of a 3-ply panel. The grains of adjacent sheets were crossed. If an open assembly time was specified, two 3-ply panels were stacked and allowed to set for a specified time. The two panels were first placed in an 11" x 11" cold press, then in an 11" x 11" hot press, again for a specified time and pressure. All manufacturing conditions specified a two-part hot pressing, whereby the pressure was lowered for the final few minutes of cure. The press conditions are shown in Figure 2-1 and Table 6-2.

Postcure Conditioning

After removal of the plywood panels from the hot press, each set of two panels was placed in a separate insulated box overnight. This ensured that each panel received identical post-cure conditioning.

Sample Preparation

After removal from the insulated boxes, the panels were trimmed. One inch was removed from each edge. The 9" x 9" panels were then cut into sixteen 1" x 4 1/2" test samples with the outer grains running along their length. Two saw kerfs were made on each sample across the outer grain, going through the outer veneer and two thirds the way through the core. They were separated by an inch and were cut on opposite sides of the sample. The samples were separated into three separate groups for testing, with adjacent samples going to different groups.

Sample Conditioning

Samples were tested in shear after conditioning in one of three methods from CSA standard 0153-M1980. Strength and wood failure were measured.

1) Dry Shear Testing. The samples were tested without any conditioning after sample cutting.

2) Boil Testing. Test specimens were submerged in boiling water for 4 hours, dried at 63°C for 20 hours, submerged in boiling water for 4 hours; then cooled in cold water. Specimens were tested wet, then dried for wood failure grading.

3) Vacuum Pressure Testing. Test specimens were submerged in cold tap water in a pressure vessel. A vacuum of 85 kPa was drawn and maintained for 30 minutes, followed by an application of pressure, 450-480 kPa for 30 minutes. The specimens were tested wet, then dried to measure wood failure.

Averaging

Thirty-two samples were broken for each test. To simplify the viewing of the data, the samples were grouped in sets of four and averaged. The samples were ordered by their wood failure grade before averaging, to preserve the visual display of the distribution. The average, standard deviation, and 90% confidence bounds were calculated using all the samples in the distribution.

CSA Specification

To pass CSA specification, in each test, the average of all specimens must be at least 80% wood failure, no more than 10% of the samples less than 60% wood failure, and no more than 5% of the samples less than 30% wood failure.

Paper Testing

White paper towels from Atlantic Packaging Products

(Scarborough, Ont.) were cut into 4.5" x 4.5" squares. The towels were dried at 100°C to remove all moisture. Glues to be tested were spread over a paper towel at 70 lbs/MDGL (2.8 grams per glue line). The glue line was surrounded with a total of seven sheets of paper towels on each side. The glue line sandwich was placed between two sheets of poplar veneer. A third piece of veneer was added to simulate a 3-ply panel. A 3-ply plywood is normally cured with 2 panels per opening. Therefore, another 3-ply panel was added without any glue. The glue-line sandwich was placed in the inner glue line which was the farthest from the hot press plates during curing. To ensure that no moisture passed between the two 3-ply panels, aluminum foil was placed between the two panels. The glue formulas are listed in Table 6-3.

The panels were cold pressed at 100 psi for 5 minutes. Hot pressing was done at 126°C and 150 psi, typically for 5 minutes but for times up to 12 minutes occasionally to study cure kinetics. After heating, the glue line sandwich was weighed to measure moisture lost during the cure. The sandwiches were then aged overnight in a desiccator for subsequent testing.

Slips, 1.5" x 0.38", were cut from the center of the

cured glue line sandwich and soaked in 10 mL of pH 12 buffer for 1 hour at 50°C. The buffer was prepared from a solution of 3.55 g/L Na_2PO_4 and 1.05 g/L NaOH.

The ultraviolet absorbance of the used buffer solution was measured at wavelengths of 220, 281, and 420 nm using a Pye Unicom UV spectrophotometer. Absorbance data was normalized by the amount of solids in the glue.

The wet glue line strips were pulled in tension to failure and an approximate measure of the fracture force obtained. The force was applied by pulling upwards at a uniform rate to a glue strip mounted on one end of a lever arm. The other end of the lever arm rested on a digital balance which recorded the force.

6.1.2 UM Lignin-PF Resin Coreaction

The lignin PF coreaction was made up as follows. The lignin PF mixture was prepared as a 3 component system containing 87.5 g of a lignin, formaldehyde, caustic mixture; 125 g of Borden W838 resin (44% solids), and 37.5 g of deionized water. This mixture consisted of 22% PF resin solids, (in effect a 1:2 dilution of PF resin alone) and had the same pH as PF resin. The

total solids content was 37%. The mixture was heated in a 70°C shaker to increase the viscosity from 68 to 350 cp. The lignin, formaldehyde, caustic mixture was prepared by combining 30.41 g of lignin, 14.84 g of 41% formaldehyde, 15.02 g of 50% sodium hydroxide, and 39.74 g of deionized water. The glue formulations are listed in Table 6-4. Glues prepared with this resin were tested on Douglas fir plywood according to vacuum-pressure test procedures.

Free Formaldehyde Assay

A 2.00 g sample containing formaldehyde (with or without lignin) was diluted with 20 mL deionized water. The mixture was adjusted to pH 9.3 with dilute sulfuric acid. Thirty mL of 0.1 M sodium sulfite was then added, which led to the formation of alkali products. The mixture was then titrated back to pH 9.3 with sulfuric acid. The moles of acid required in the titration were equivalent to the moles of formaldehyde in the original sample, as shown in the standard curve of Figure 6-1. The presence of lignin did not interfere with the assay.

UM Lignin - PF Resin Synthesis

Resin Preparation:

A lignin-free PF resin preparation contained formaldehyde (37% w/w), phenol (90% w/w), sodium hydroxide (50% w/w) and water in amounts of 805 g, 471 g, 90 g, and 468 g, respectively. The vessel used for resin synthesis was a 5 L, three neck flask. A cooling coil, stirrer, and condenser/thermometer occupied the three posts. To prepare a resin, the ingredients were mixed together prior to heating. Some caustic was reserved for addition later in the heating cycle. The temperature was controlled by a heating mantle activated by a temperature probe, and by the cooling coil containing cold water. A stirrer driven by an electric motor was used to ensure proper mixing. Samples were taken at approximately 20 to 30 minute intervals. Viscosity was determined at 25°C. Two aliquots of sodium hydroxide were added when the mixture reached a viscosity window of 1000 to 2000 cp. Initial temperature was set at 85°C and adjusted to 75°C after the first caustic spike.

A heating cycle and ingredient profile was adopted for each of the systems containing lignin, unmodified or otherwise. However, all of the systems were based on the lignin-free PF resin preparation. Figure 2-25 shows the viscosity profile typical of a regular PF

resin prepared at Iogen.

The same apparatus used to prepare PF resin was used to prepare lignin PF resin. Into the three neck flask was added 571 g of 37% (w/w) formaldehyde, 236 g of 90% (w/w) phenol, 90 g of 50% (w/w) sodium hydroxide, 240 g of Steam-Exploded Lignin, and 468 g of water. Two more aliquots of 50% w/w sodium hydroxide were prepared for later addition, 72 g and 54 g. These aliquots were added when the mixture reached the appropriate viscosity. This resin was tested in a commercial glue formulation on Douglas fir veneer. Vacuum pressure test conditions were maintained. Glue formulations can be found in Table 6-5.

6.2 Chemical Modifications to Lignin

6.2.1 Hydroxymethylation Reaction

A 1% lignin solution was made in buffer. A 1 M sodium hydroxide and a 1/2 M sodium bicarbonate solution was mixed 1:3 for buffer at pH 10.0, 1:2 for pH 10.5, and 1:1 for pH 11. The buffer was added such that the sodium hydroxide concentration was 3% sodium (w/w) on lignin. The mixture was allowed to equilibrate overnight at the reaction temperature of 70 or 85° C. The solution was filtered to remove any residual cellulose and the pH was adjusted to the reaction pH before formaldehyde was added. A 5% formaldehyde solution was added to give the desired formaldehyde to lignin ratio. The system was purged with nitrogen (unless otherwise specified) and kept at temperature for the desired time. Laboratory samples were prepared in 250 mL flasks; larger scale samples in 14 L NBS fermenters. For testing in phenol formaldehyde glues, the lignin was acid precipitated to pH 2, filtered, reslurried, and filtered a second time to wash out the buffer. The lignin was dried overnight in a 100° C oven, then ground into a powder and passed through a 200 mesh screen. Using independent variables of temperature, pH, formaldehyde dosage, and aeration, six lignins were produced of which five were hydroxymethylated. The other lignin was a

control. Table 4-1 gives the conditions for each treatment.

Measurement of Formaldehyde Uptake

Direct

In the direct method, the percent insoluble solids was compared before and after formaldehyde treatment. The difference in weight, was taken to be indicative of formaldehyde uptake.

Indirect Method

In the indirect method, formaldehyde uptake was calculated from assay results of free formaldehyde (Walker, 1970) and formic acid. According to the Canizzaro reaction, an aldehyde in a high pH environment will break down to an acid and an alcohol. In the case of formaldehyde, the Canizzaro products are formic acid and methanol. An assay to measure free formaldehyde was modified for use in the lignin system. Assay results of formaldehyde standards in buffer and in an acid precipitated lignin buffer filtrate are shown in Figure 6-1. The relationship between free formaldehyde added and the amount measured is linear over a free formaldehyde concentration up to 1.2%. At 0% formaldehyde added, a small amount of free formaldehyde was measured, which was subtracted from all measurements. The presence of residual, soluble lignin did not affect the assay results.

Formic acid was measured by two methods. In the first method, a sample of lignin/formaldehyde slurry was pH adjusted up to the pH of a control lignin slurry not containing formaldehyde (i.e. no formic acid). The rationale for using this assay was that the amount of formic acid produced is a function of the drop in pH. In the second method, formic acid was measured by absorbance (Sleat and Mah, 1984). The lignin was first acid precipitated and filtered. A sample of the filtered liquid was mixed with assay reagents and the absorbance of this mix compared to a standard curve.

A formic acid standard curve was prepared (Figure 6-2) over a range of 0 to 1 gram per litre. A linear relationship was shown and the assay results, in triplicate, showed good reproducibility.

6.2.2 Phenolation

Lignin:

The primary substrate was Iogen Steam-Exploded Lignin that was precipitated in dilute sulfuric acid (Methoxyl content 16.65%, batch number UM081AAC). Commercial solid lignin substrates included Indulin AT Kraft lignin from Westvaco which is 5% moisture, and Reed Lignosulfonate SF (Reed, Quebec, P.Q.), which is 7% moisture. Spent sulphite liquor

from softwood and hardwood was obtained from Temfiber (Temiscaming, P.Q.) and contained 20% solids. The solids fraction consisted of 85% ammonium lignosulfonate and 15% sugar. The predominant sugar was xylose in the hardwood sample and mannose in the softwood sample.

Phenol Assays:

Phenol was assayed by taking advantage of its unique absorption properties that distinguish it from lignin. Samples (1 g) were diluted with 14 mL deionized water. The pH was adjusted to 2.5 with a measured volume of 1 N sulfuric acid, typically about 1 mL. The mixture was then vacuum filtered to remove any precipitated lignin. The filtrate was further diluted (about 1/200) with deionized water and the absorbance measured at 240 and 270 nm with a Pye Unicam SP6-550 UV/vis spectrophotometer. The undiluted absorbance of the sample is:

$$A_{un} = A_{dil} D_f \left(\frac{V_s + V_a + V_w}{V_s} \right) \qquad (1)$$

where A_{un} = Undiluted absorbance of sample (at 240 or 270 nm)

A_{dil} = Observed (diluted) absorbance

D_f = Dilution of filtrate

V_s = Volume of sample, mL

V_w = Volume of water in first dilution, mL

V_A = Volume of sulfuric acid solution added, mL

Equation (1) neglects the small loss of volume caused by the removal of lignin precipitate. The undiluted absorbances A_{UN} were correlated with the phenol concentration as follows. The lignin and phenol stock solutions were diluted with deionized water to 0-1 g/L solids concentration. Absorbance measurements generated standard curves for 240 and 270 nm which are linear. The standard curves for phenol and Exploded Wood lignin are shown in Figure 6-3. The absorbance of a sample containing lignin and phenol is the sum of the separate absorbances, assuming that there are no net interfering or synergistic signals. Therefore,

$$A_{270} = P \times A^{P}_{270} + L \times A^{L}_{270} \quad (2)$$

$$A_{240} = P \times A^{P}_{240} + L \times A^{L}_{240} \quad (3)$$

where A_{270} and A_{240} = Undiluted absorbances at 270 and 240 nm, respectively

P = Free phenol, g/L

L_p = Soluble lignin, g/L

A^P_i and A^L_i = Specific absorbance of phenol and lignin, respectively, at wavelength i, absorbance /(g/L)

The specific absorbances are given by the slopes of the standard curves of absorbance as a function of concentration, as shown in Figure 6-3. The specific absorbances of the substrates used in this study are summarized in Table 6-6.

The concentration of phenol is given by determining the appropriate specific absorbances and combining equations (2) and (3). The result is:

$$P = \frac{A^L_{240}A_{270} - A^L_{270}A_{240}}{A^L_{240}A^P_{270} - A^L_{270}A_{240}} \quad (4)$$

As a test of this method, several mixtures of Exploded Wood lignin and phenol were mixed and assayed for phenol concentration. The resulting "dead soldier plot" of the assayed and actual concentrations agrees well, as shown in Figure 6-4.

6.3 Chemically Modified Lignin in Plywood Glues

6.3.1 Hydroxymethylated Lignin

Direct Addition

HM lignin was added directly to a commercial glue formula substituting for 50% PF resin. This lignin had been previously dried, crushed and passed through a 200 mesh screen. Typically, as with UM lignin, the powder is simply added together with the rest of the solid ingredients. However, mixing problems occurred with the treated lignins (both processed with and without formaldehyde). Upon addition of the lignin with the rest of the ingredients, the glue became viscous and lumpy. By mixing the water and the lignin first, followed by the addition of the other powdered ingredients, the difficulties were lessened somewhat. It is thought that these difficulties may have occurred due to processing conditions. The lignin was acid precipitated prior to filtering and washing and may have remained somewhat acidic even after washing. Mixing of an acidic ingredient with the resin (pH 13.3) would result in a precipitate.

These glues were tested on Douglas fir according to vacuum/ pressure test conditions. A list of the ingredients loadings (lbs/MDGL) is given in Table 6-7.

HM-PF Resin

Into the three-neck flask of the resin apparatus was added 430 g of water, 215 g of HM lignin (92.9% w/w), 528 g of formaldehyde (42.7% w/w), 223 g of phenol (90% w/w) and 85 g of sodium hydroxide (50% w/w). The flask was heated to 80°C until the first viscosity window was reached (1000 cp). At this time 68 g of sodium hydroxide (50% w/w) was added. The temperature was turned down to 70°C. When the viscosity reached 450 cp the final caustic spike (51 g of 50% w/w) was carried out. The reaction contents were cooled and refrigerated.

The resin was used in a plywood glue formula and compared with a commercial glue and a lignin control glue. The PF resin solids plus lignin were the same for the HM lignin resin and the commercial glue. Filler ingredients (cocob, wheat flour, soda ash, RX-100) were adjusted proportionately for the HM lignin resin in order that the final viscosity of the glues was the same (1800-2500 cp).

Douglas fir plywood was prepared with the three glues. Samples were tested according to vacuum/pressure procedures. Glue formulations can be found in Table 6-8.

6.3.2 Phenolated Lignin

Direct Addition

Phenolated lignin (caustic soluble and insoluble fractions) was ground and passed through a 200 mesh screen. Plywood glue was prepared with each lignin by adding a fixed amount to a commercial glue formula. Water was added to adjust the viscosity to the proper range. A commercial glue and a lignin control glue were also prepared. Each glue was used to make Douglas fir plywood. Vacuum/pressure test procedures were used. Table 6-9 gives the glue formulations of the tested glues.

Phenolated Lignin-PF Resin

Into a 5 L resin vessel was added 1464 g of phenolated lignin mixture prepared in the pilot plant scale-up and 226 g of paraformaldehyde. The composition of the starting mixture was 12.2% phenol (phenol bound to lignin and free phenol), 12.2% lignin, 10.7% formaldehyde, 6% sodium hydroxide, and 58.7% water. Two aliquots of 50% w/w sodium hydroxide, 68 g and 54 g, were set aside for later addition. Glues prepared with phenolated lignin PF resin were tested on Douglas fir according to vacuum/pressure test conditions. Formulation of these glues is given in Table 6-10.

6.3.3 Alkali-Treated Lignin

Alkali Treatment:

Unmodified lignin (UM081AAC) which was acid precipitated was treated with sodium hydroxide at a concentration of 10% (w/w) on lignin. Two temperatures were used; 70°C and 150°C. At each temperature, the reaction was run for 6 hours both in the presence of oxygen and in an oxygen-free atmosphere.

A batch solution was prepared containing sodium hydroxide (2%), water (88%) and lignin (10%). The batch solution was divided and half was heated in a Parr reactor at 150°C. The remaining solution was heated at 70°C in a Brunswick shaker.

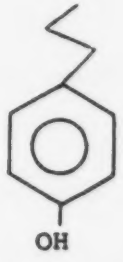
The two lignins treated in an oxygen-free environment were done so using degassed water. The reaction vessels were purged of oxygen using N_2 gas prior to heat treatment.

The alkali treated lignins were isolated by diluting the reactants with water and pH adjusting to 1.90 with H_2SO_4. After warming, the precipitated lignin was filtered and washed with deionized water. The filter cake was dried at 100°C overnight, and ground to a powder. The powder was passed through a 200 mesh screen.

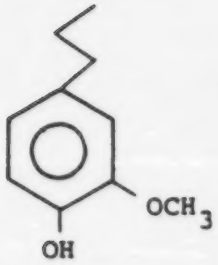
Plywood glues were prepared with the alkali treated lignin substituting for 50% of the PF resin of a commercial glue. Two lignin controls were also tested. The first was an acid precipitated lignin having a light caustic treatment and the other an unmodified lignin. Both lignins were powders. Douglas fir veneer was used, and was tested according to vacuum/pressure test procedures. Glue formulations can be found in Table 6-11.

FIGURE 1-1a **CONSTITUENTS OF STEAM-EXPLODED LIGNIN**

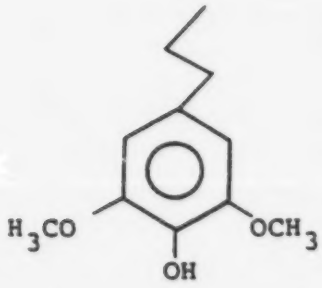
Phenol



Lignin: p-Hydroxyphenyl Group

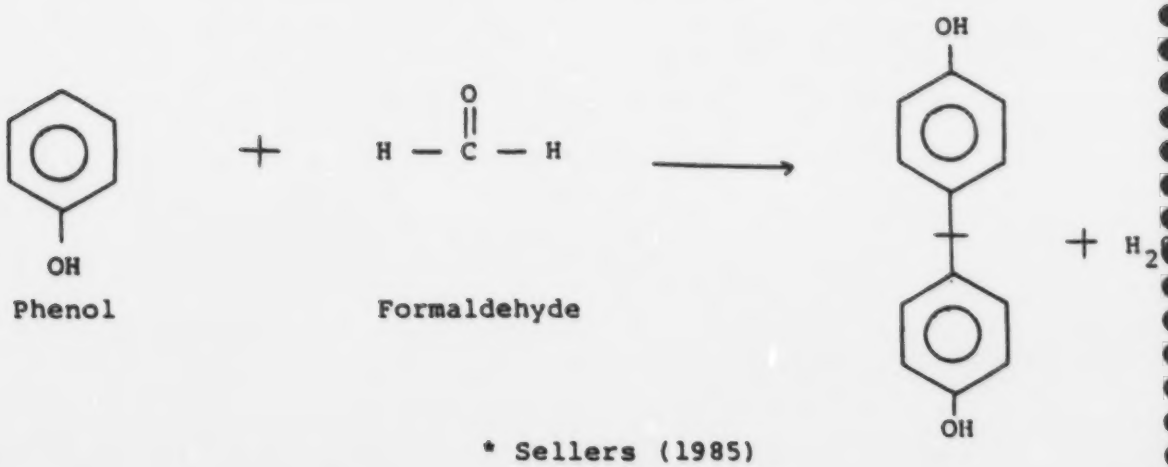


Lignin: Guaicyl Group



Lignin: Syringyl Group

FIGURE 1-1b **PHENOL FORMALDEHYDE REACTION***



Phenol

Formaldehyde

* Sellers (1985)

FIGURE 1-2 COMMERCIAL GLUE FORMULATION

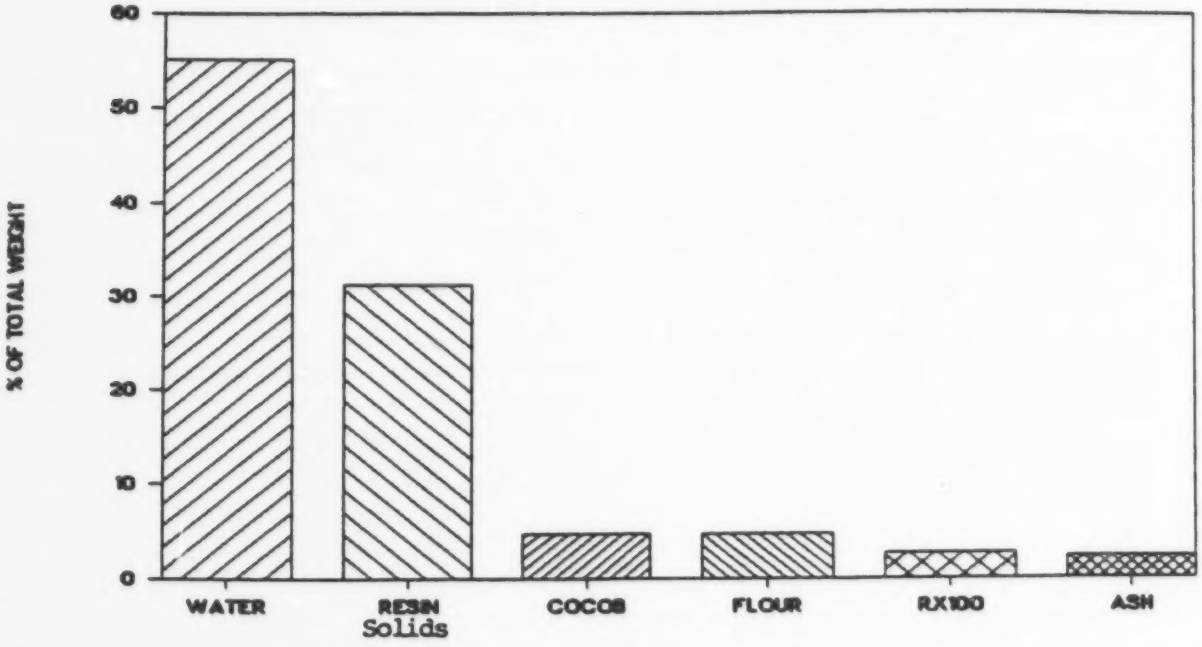


Figure 1-3: THE USE OF LIGNIN IN PLYWOOD ADHESIVES

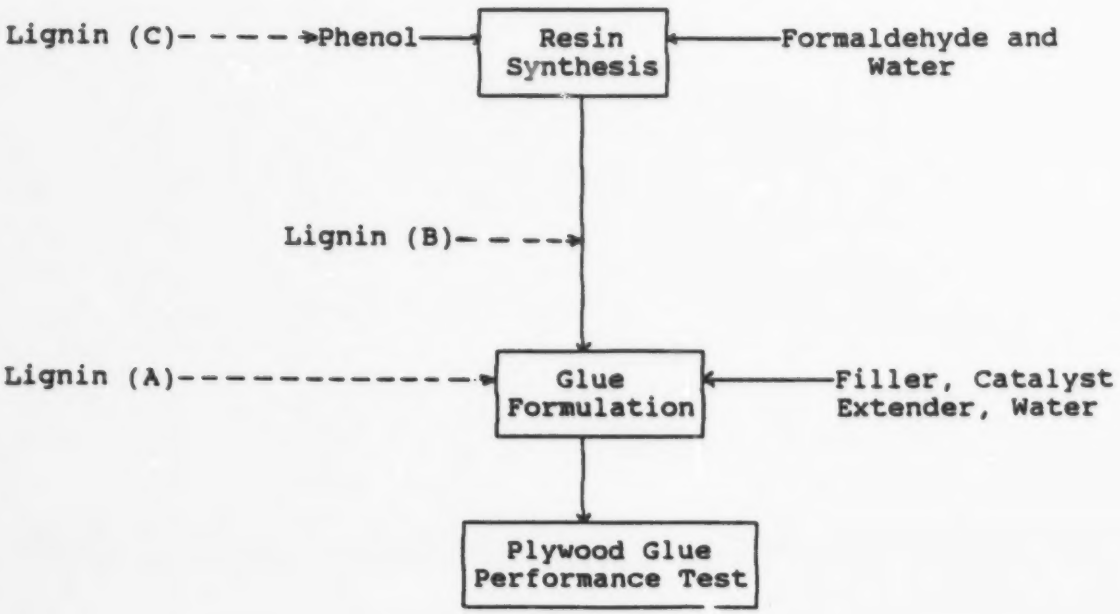
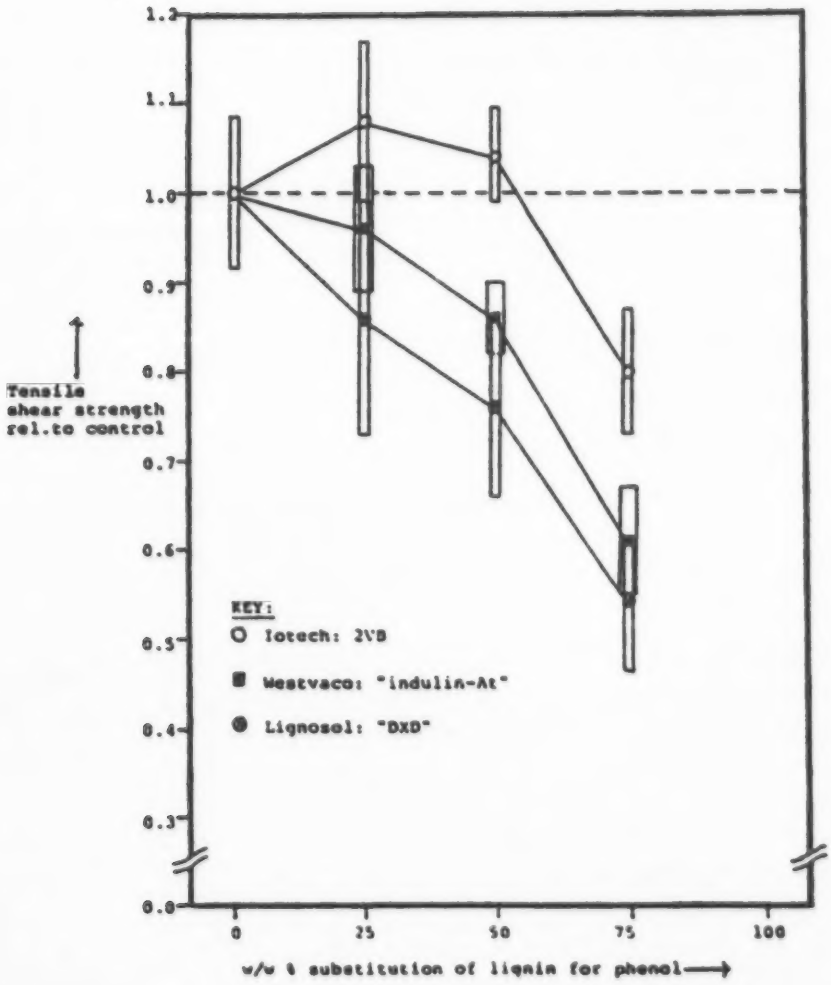


FIGURE 1-4 TENSILE SHEAR STRENGTH OF GLUE JOINTS VERSUS LEVEL OF SUBSTITUTION *



* Foody and McGuire (1986)

FIGURE 2-1: PREPARATION OF PLYWOOD

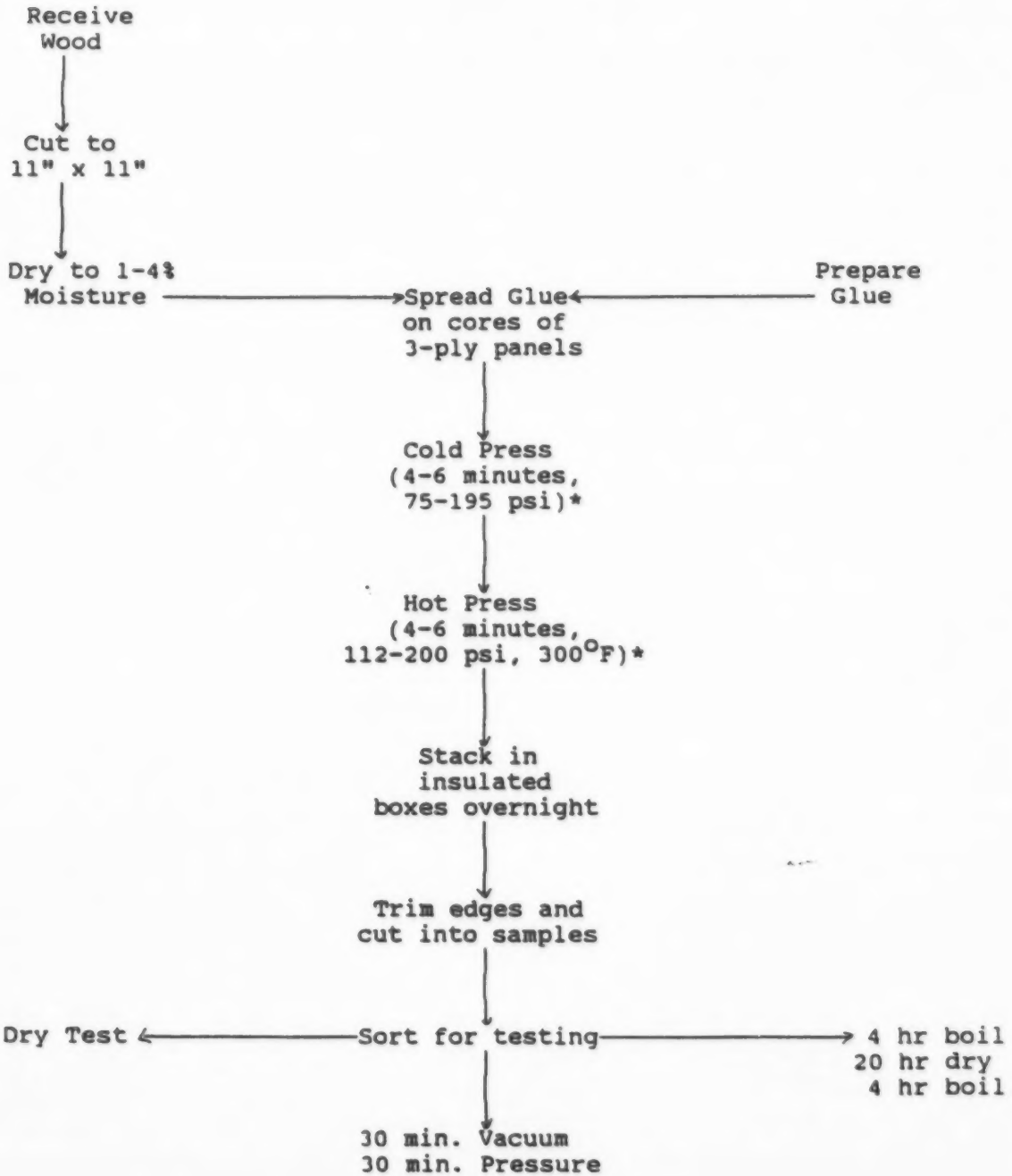

Receive Wood
Cut to 11" x 11"
Dry to 1-4% Moisture
Prepare Glue
Spread Glue on cores of 3-ply panels
Cold Press (4-6 minutes, 75-195 psi)*
Hot Press (4-6 minutes, 112-200 psi, 300°F)*
Stack in insulated boxes overnight
Trim edges and cut into samples
Sort for testing
Dry Test
4 hr boil
20 hr dry
4 hr boil
30 min. Vacuum
30 min. Pressure

Figure 2-2 COMPOSITION OF DOUGLAS FIR GLUES

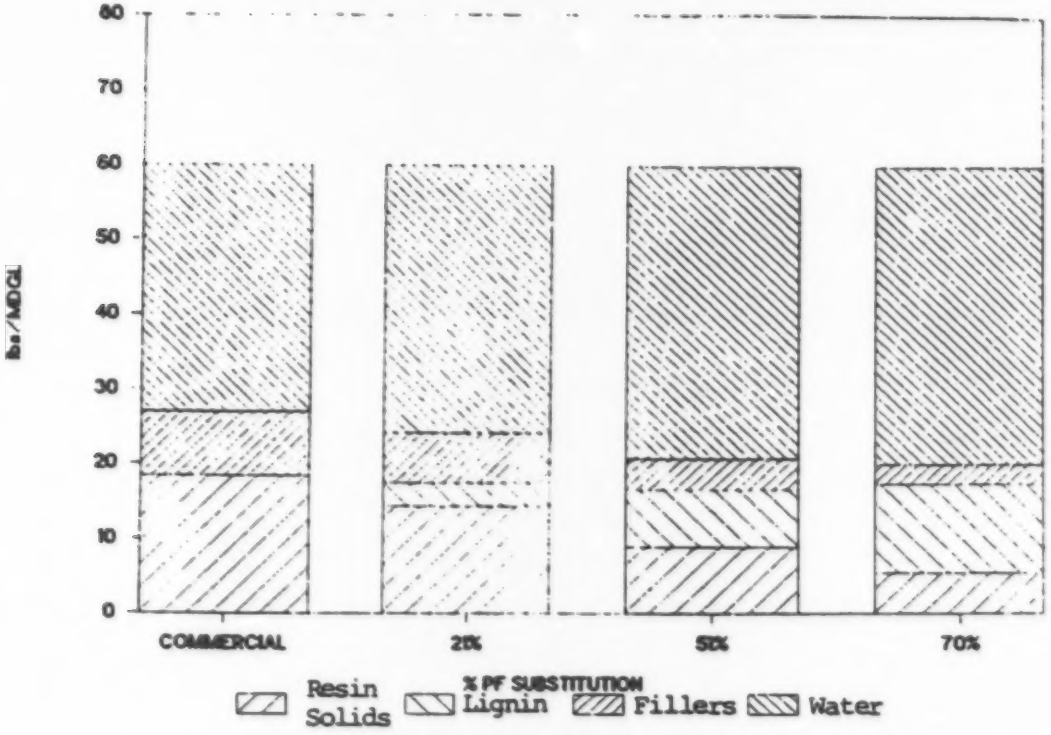


Figure 2-3 COMPOSITION OF POPLAR GLUES

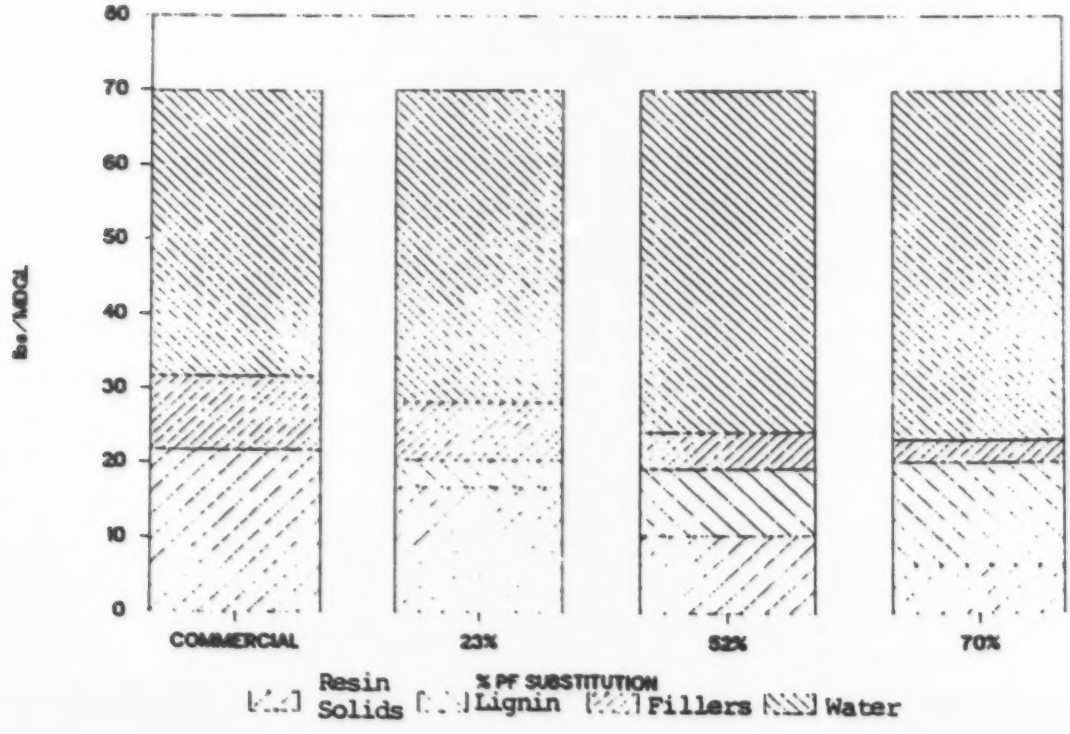


Figure 2-4 COMPOSITION OF SPRUCE GLUES

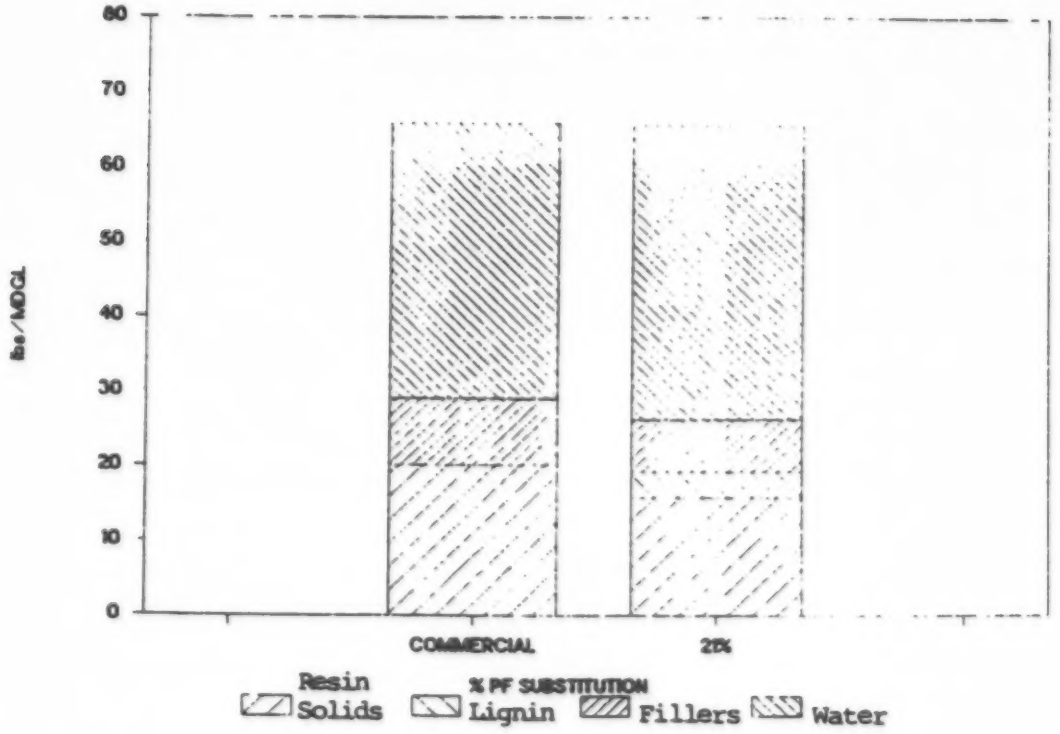


FIGURE 2-5: DOUGLAS FIR RESULTS

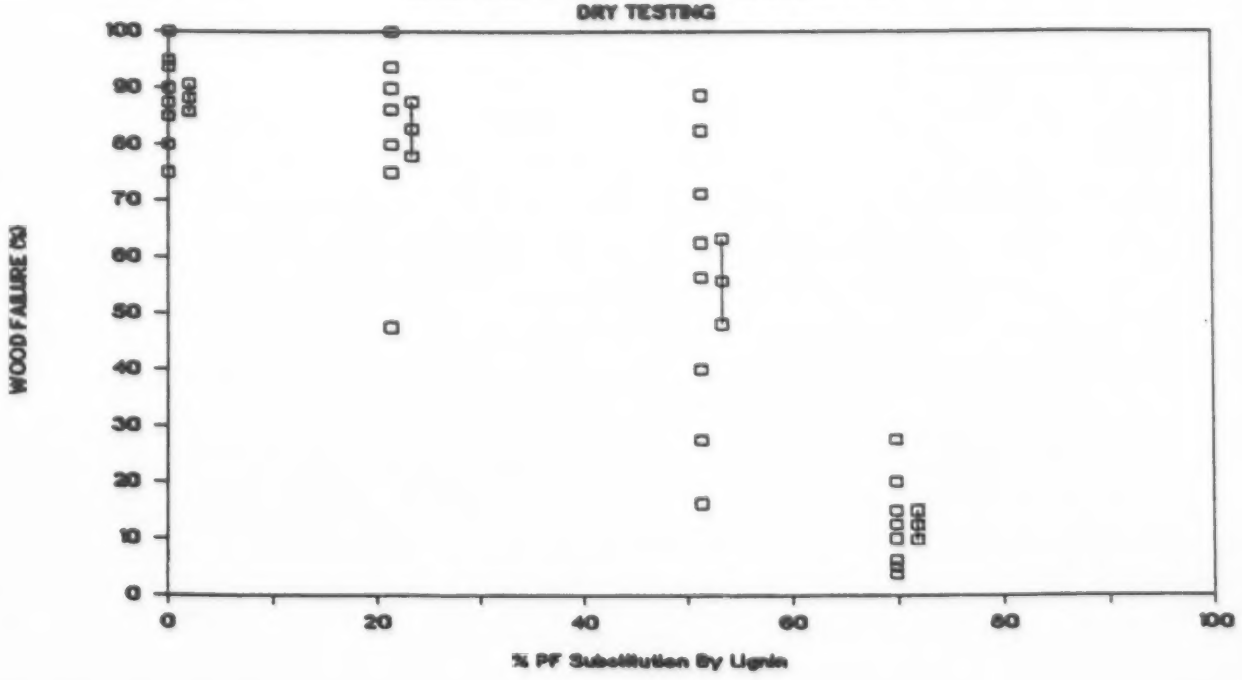


Figure 2-6 DOUGLAS FIR WOOD FAILURE RESULTS

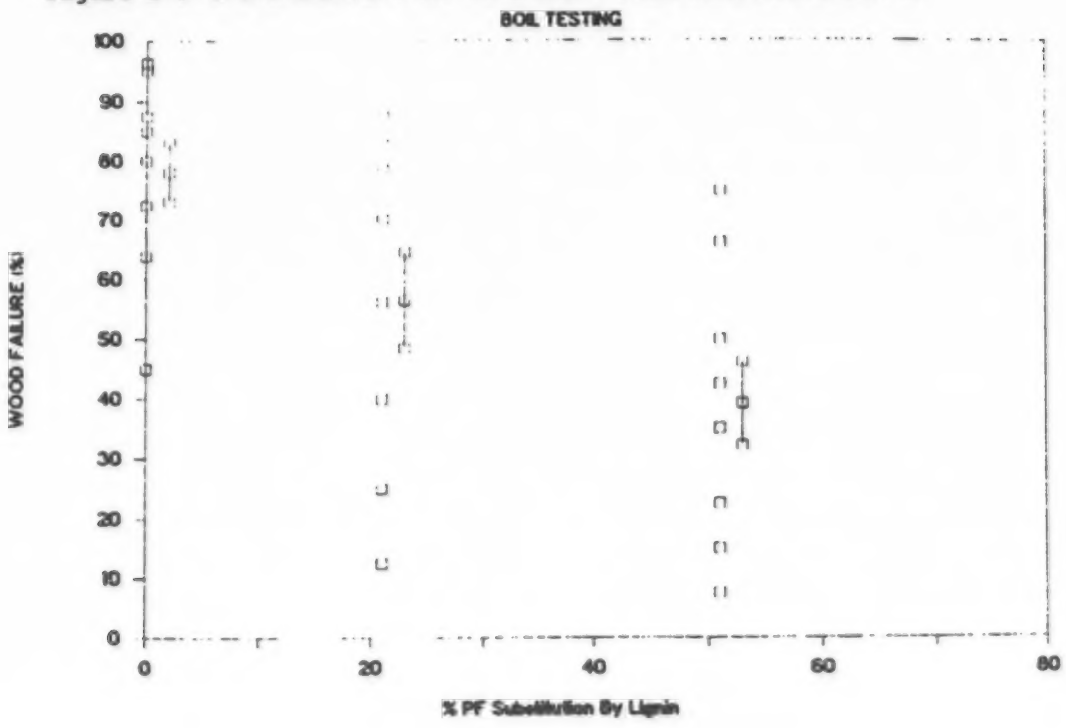


Figure 2-7 DOUGLAS FIR WOOD FAILURE RESULTS

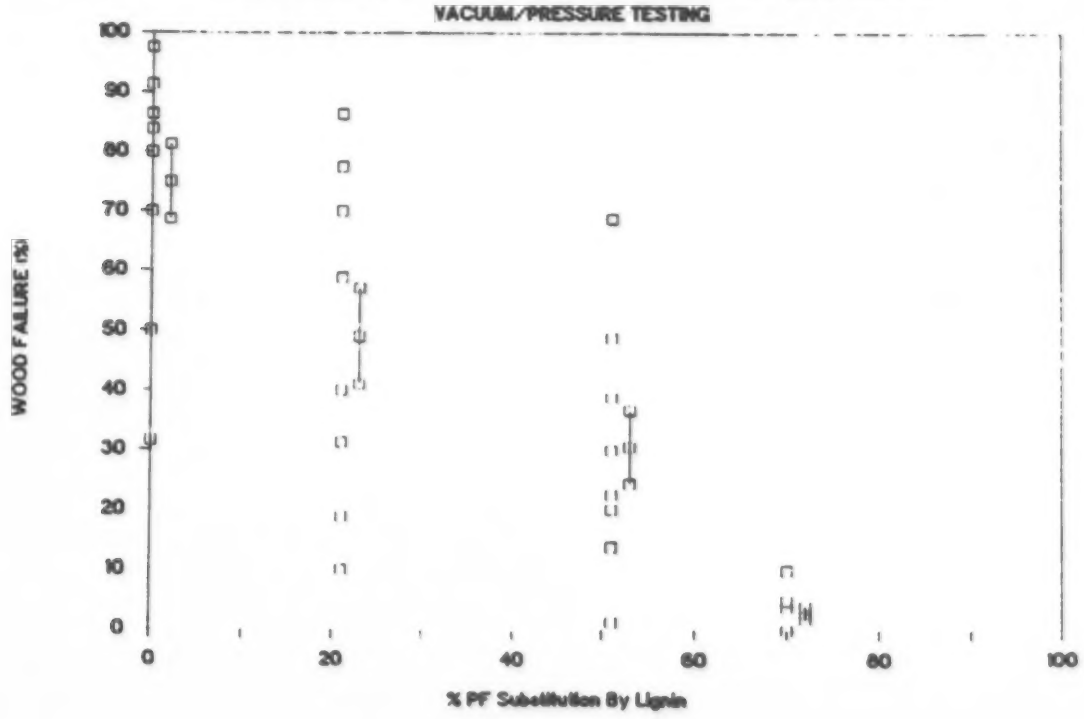


FIGURE 2-8:

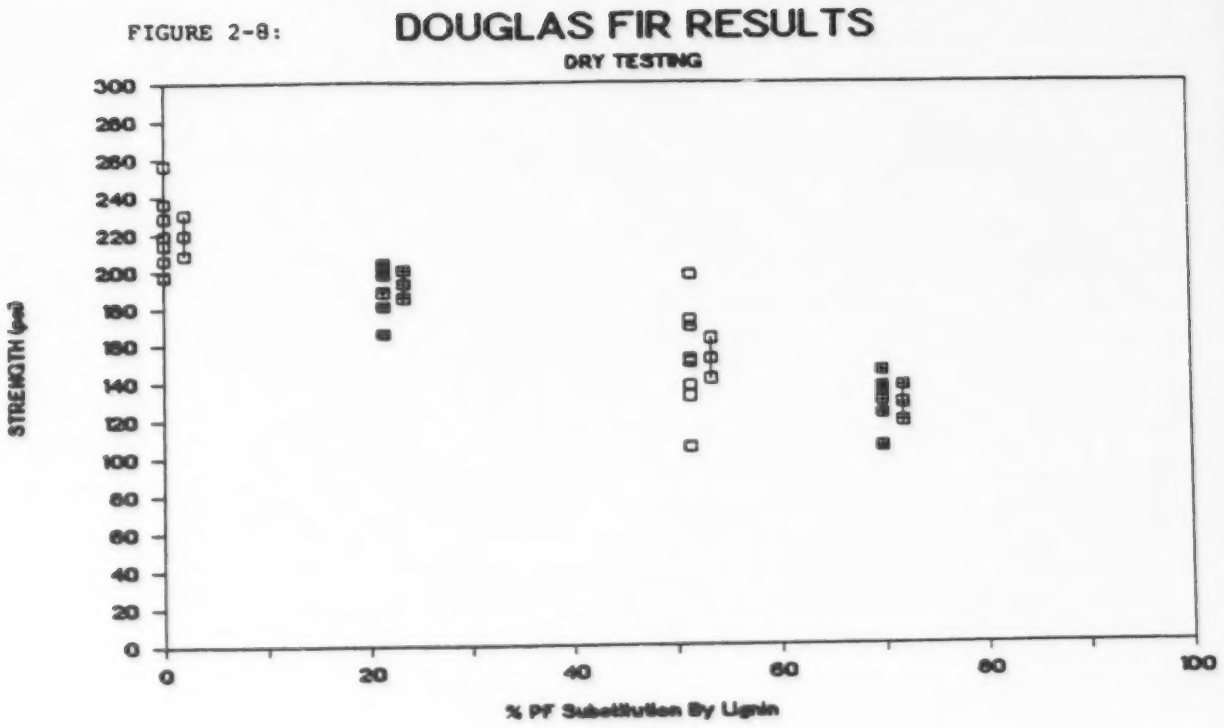


Figure 2-9

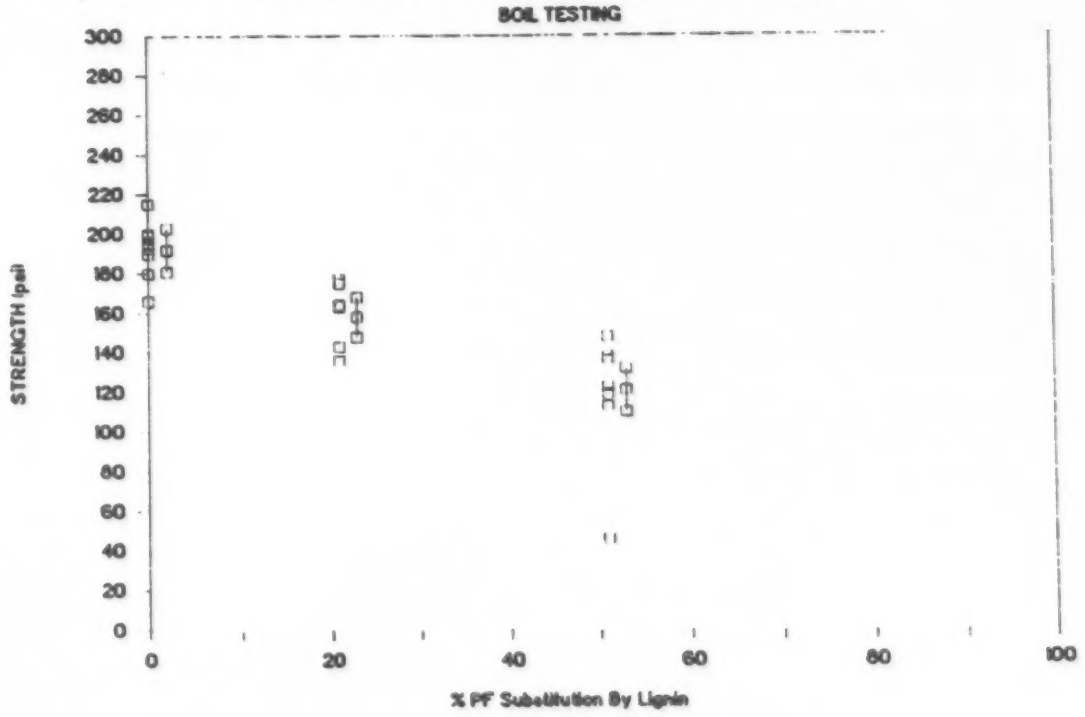


Figure 2-10 DOUGLAS FIR STRENGTH RESULTS

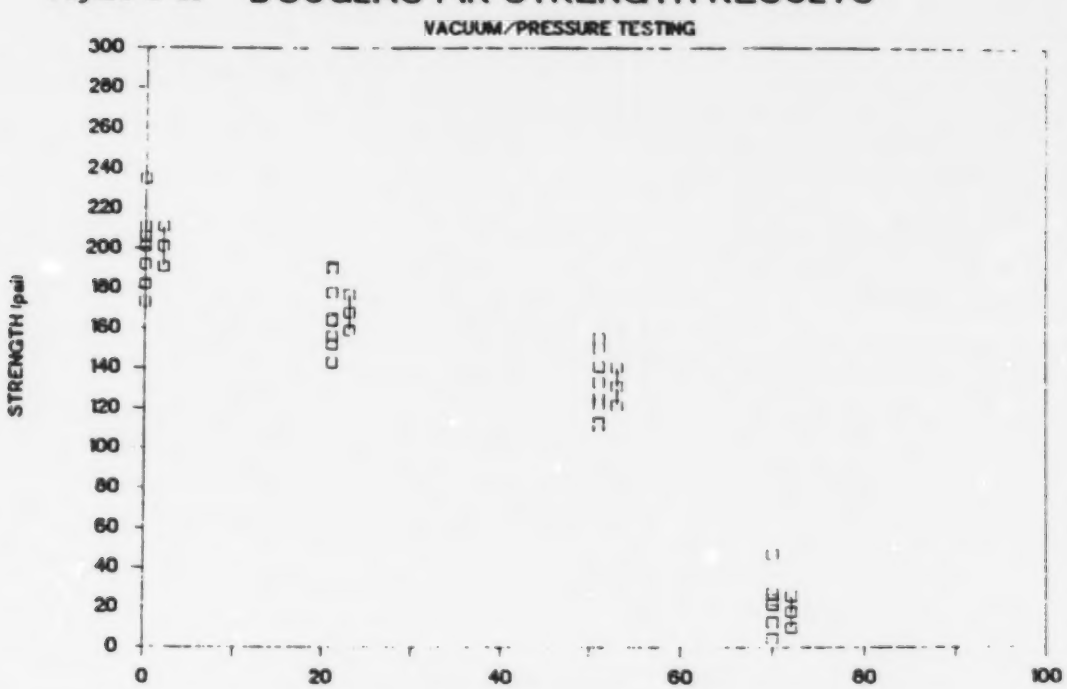


FIGURE 2-11: POPLAR WOOD FAILURE RESULTS

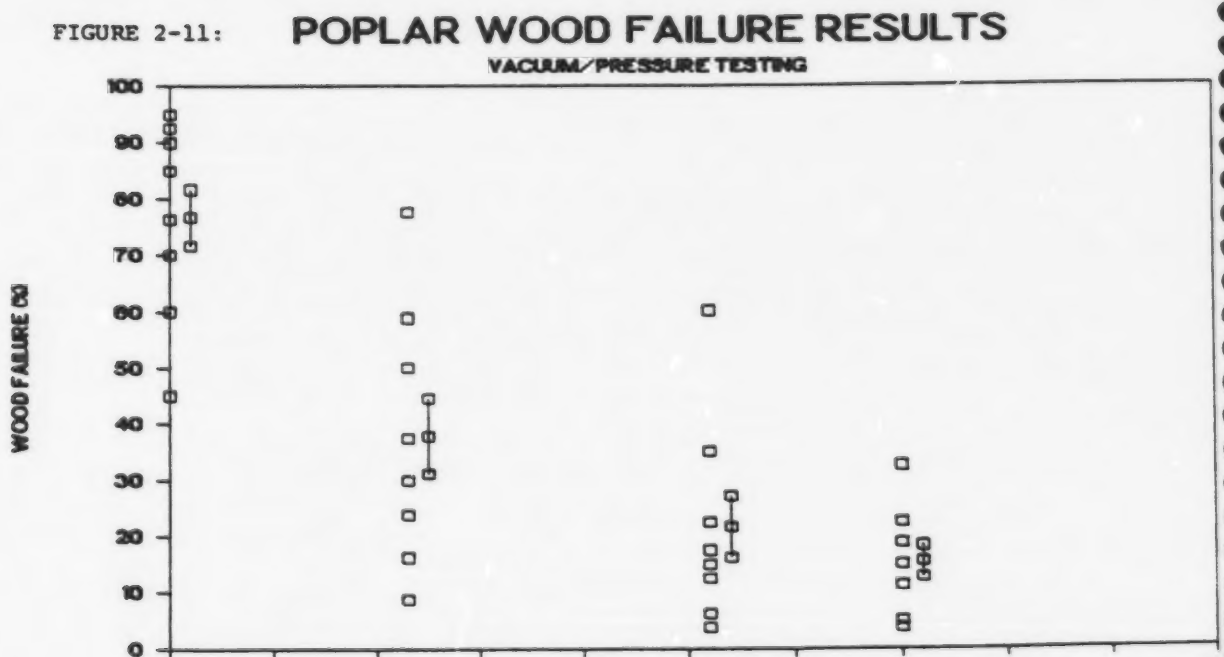


Figure 2-12

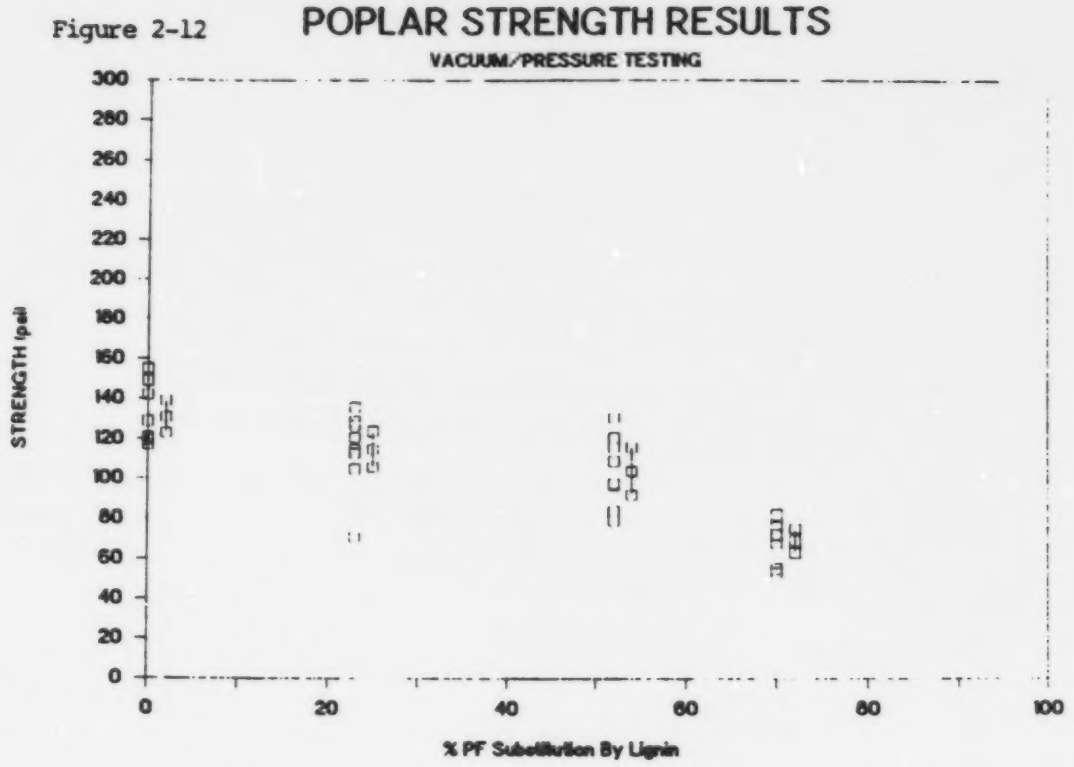


FIGURE 2-13:

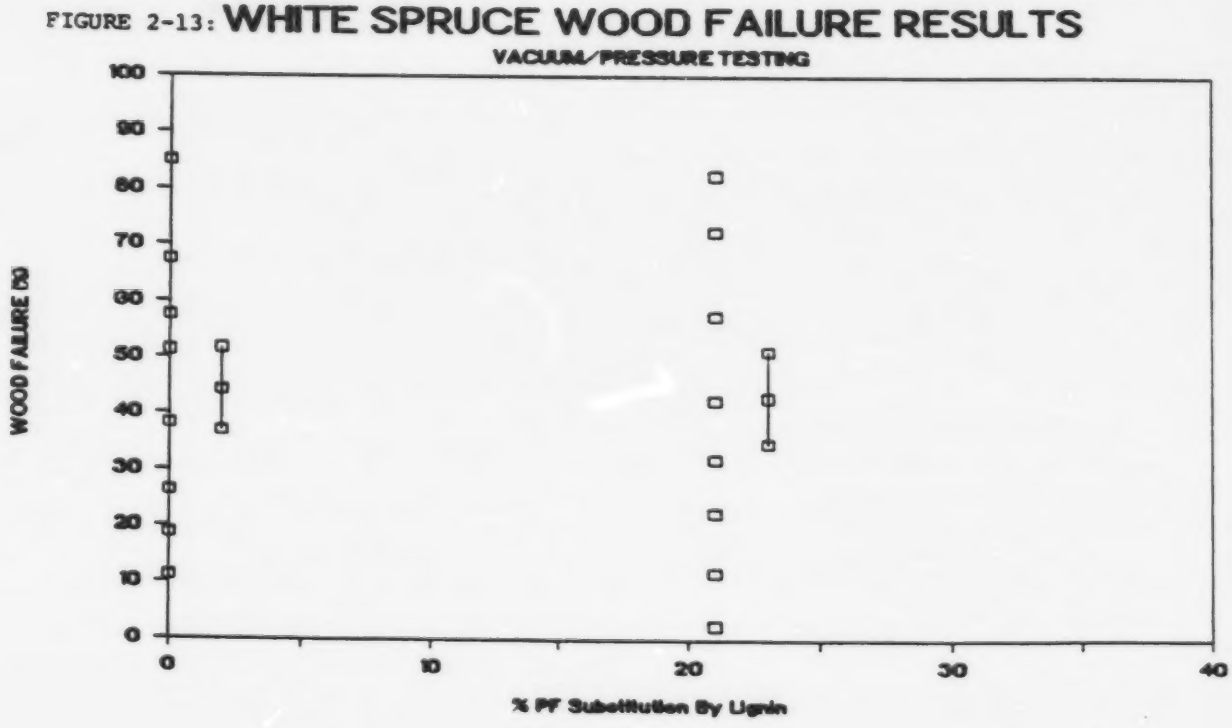


Figure 2-14 WHITE SPRUCE STRENGTH RESULTS

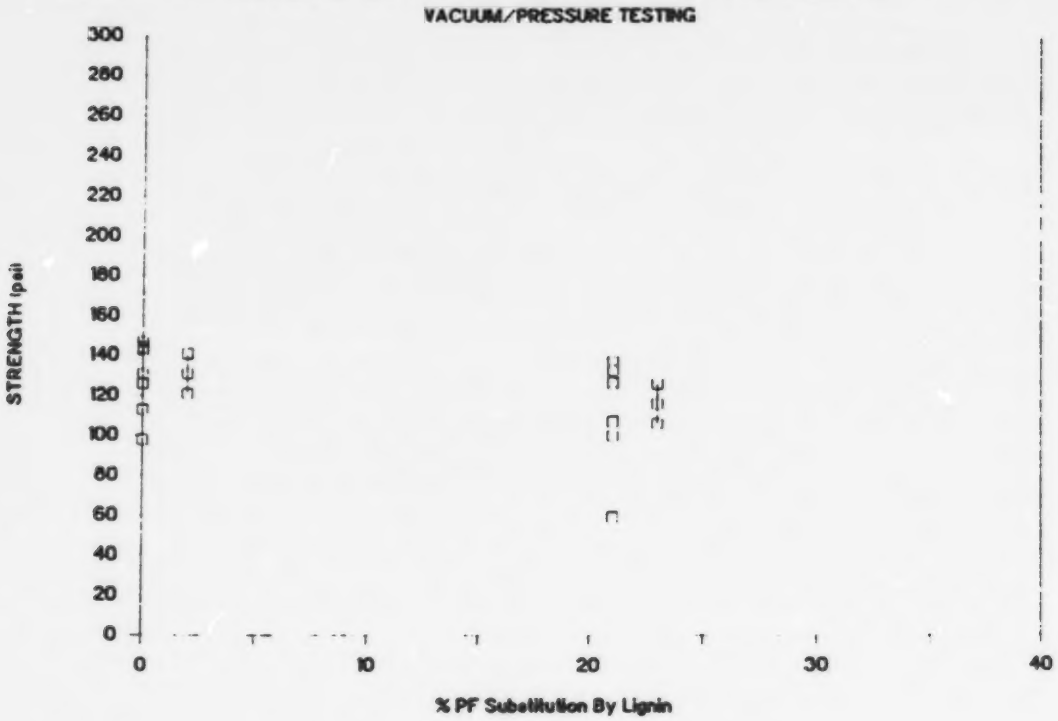


FIGURE 2-15: DIAGRAM OF PAPER TEST

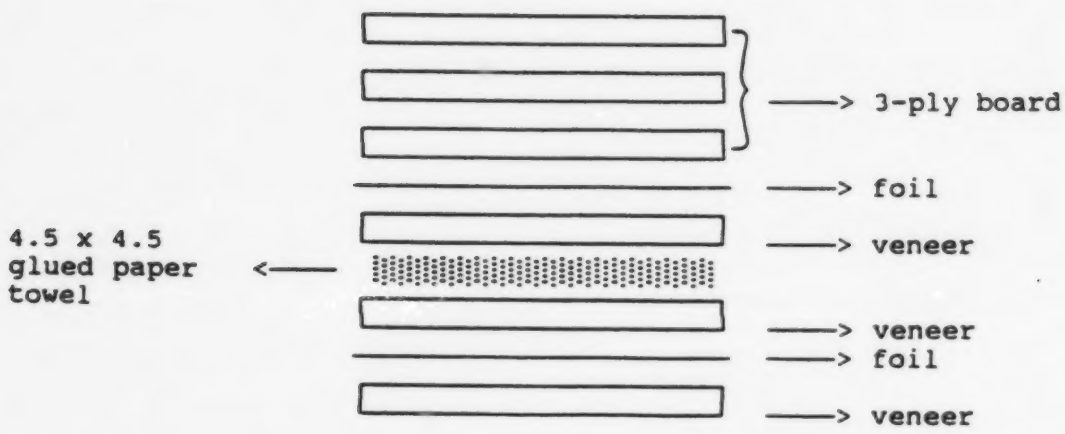


Figure 2-16 PAPER TEST GLUE COMPOSITIONS

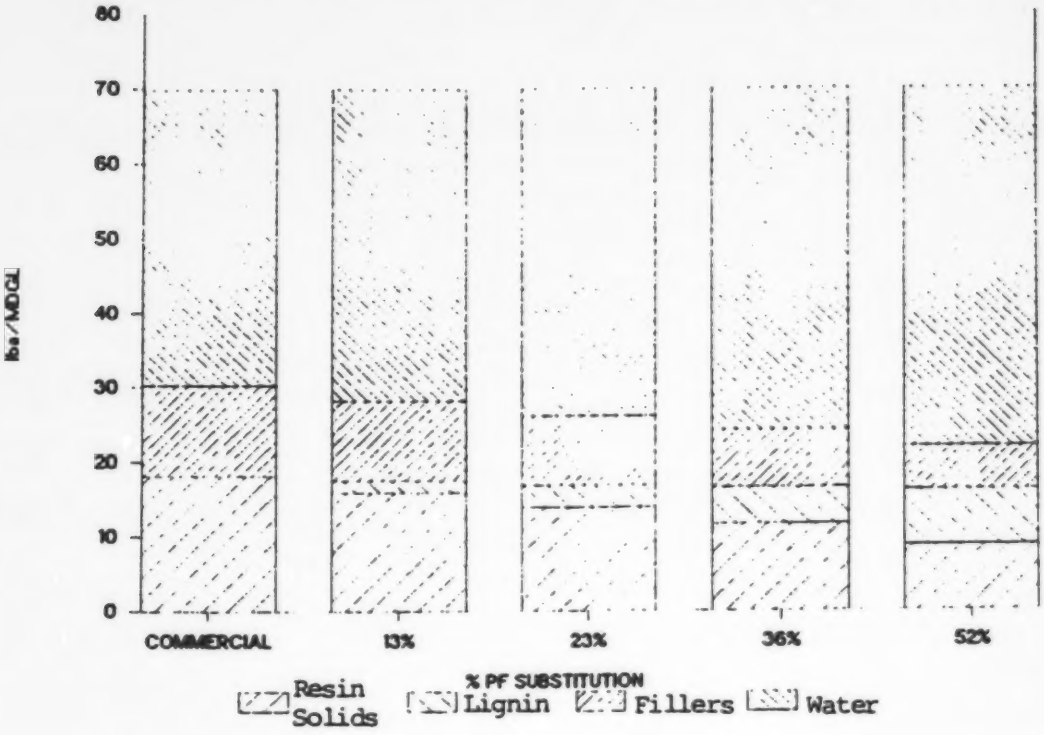


FIGURE 2-17: PAPER TEST MOISTURE REMOVAL

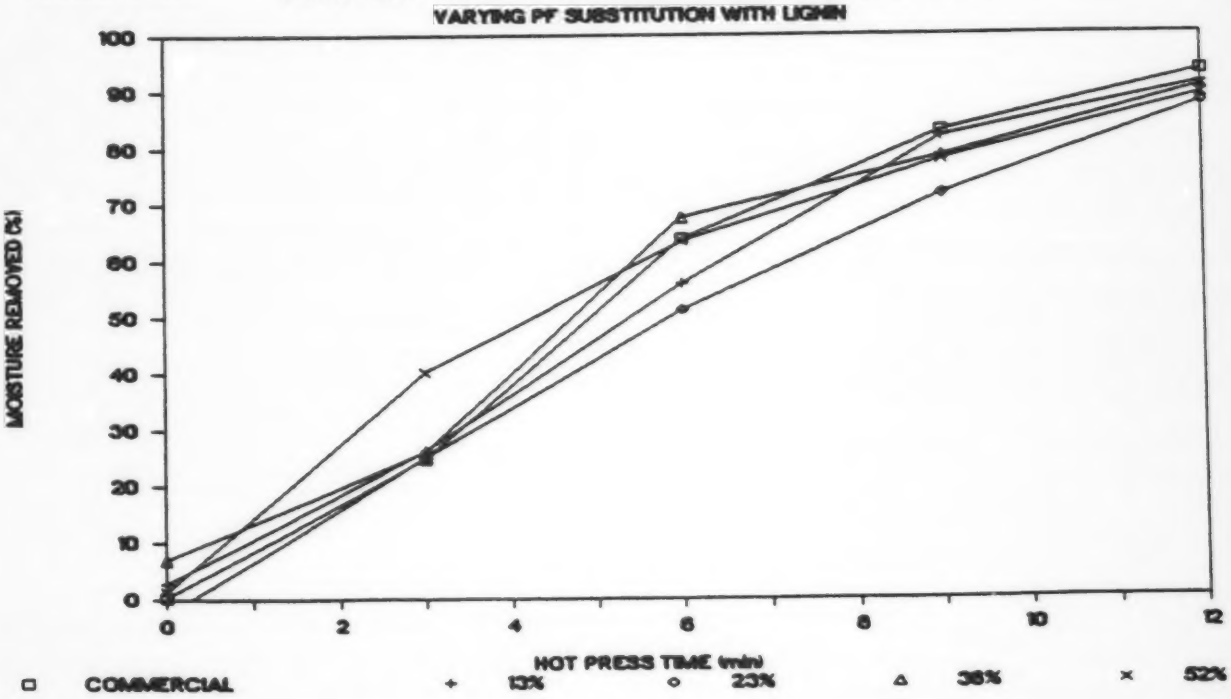


FIGURE 2-18: PAPER TEST GLUE SOLIDS CONTENT

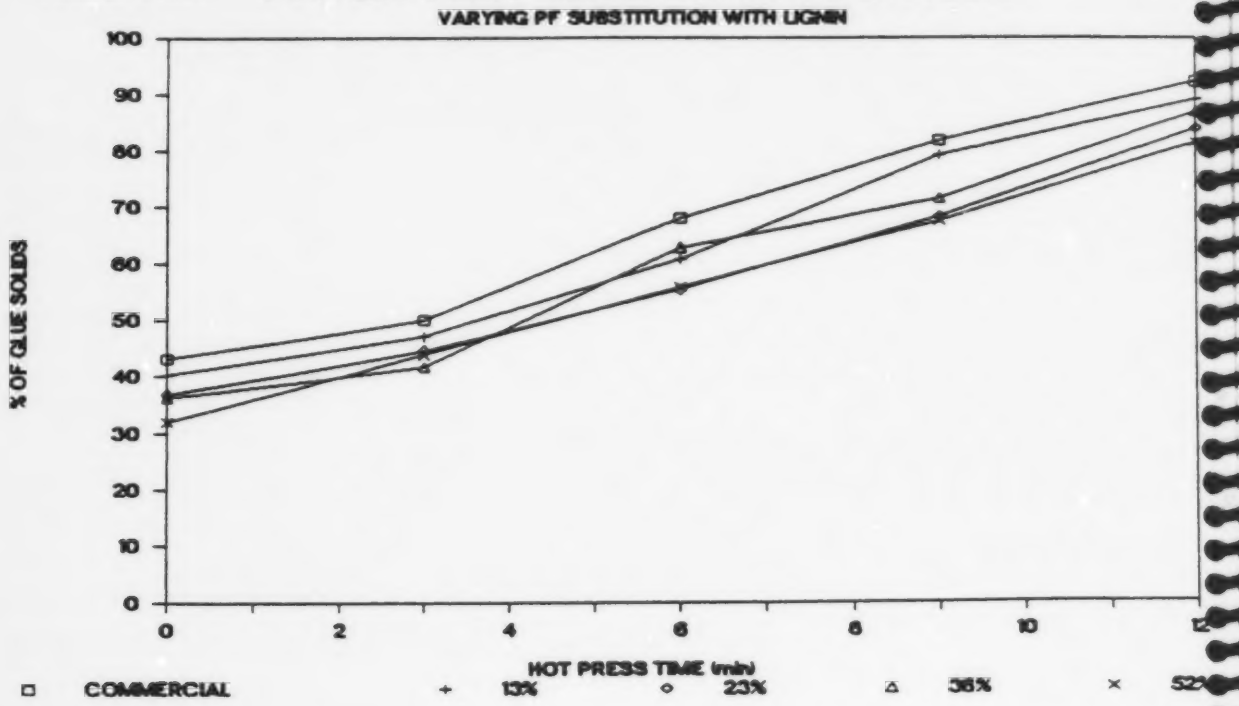


FIGURE 2-19: PAPER TEST STRENGTH RESULTS

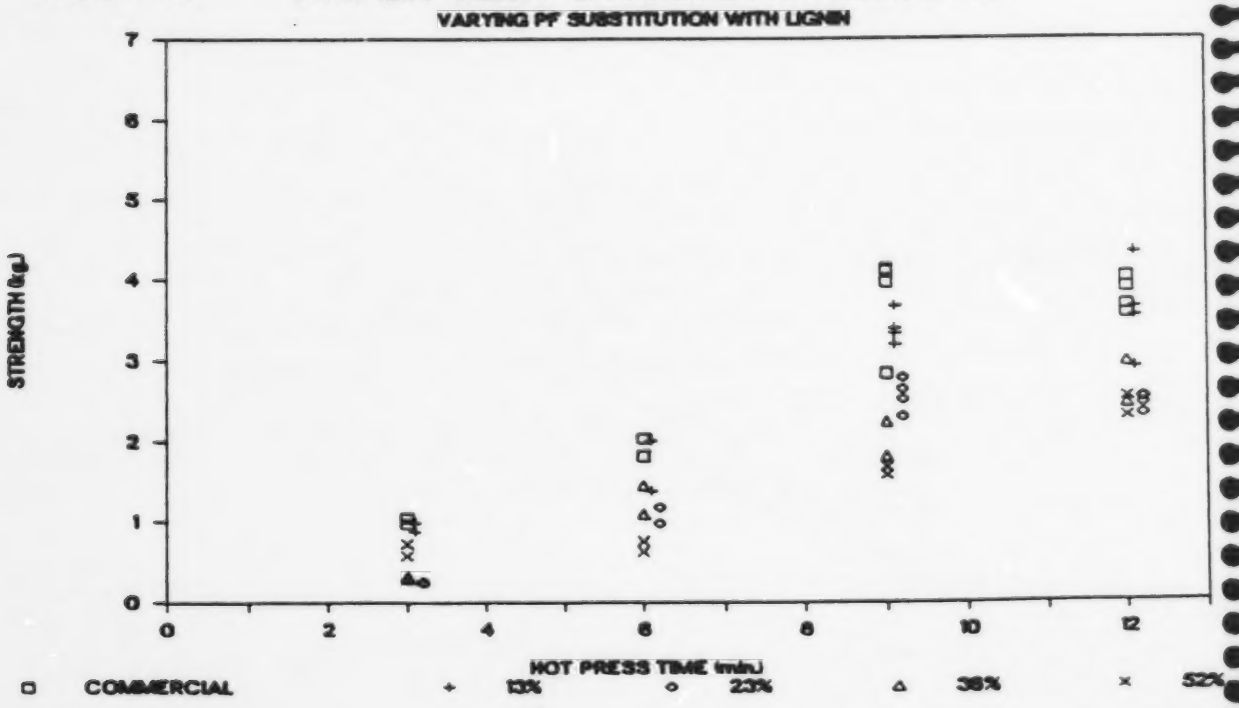


FIGURE 2-20: VISCOSITY PROFILE OF CO-REACTED RESIN

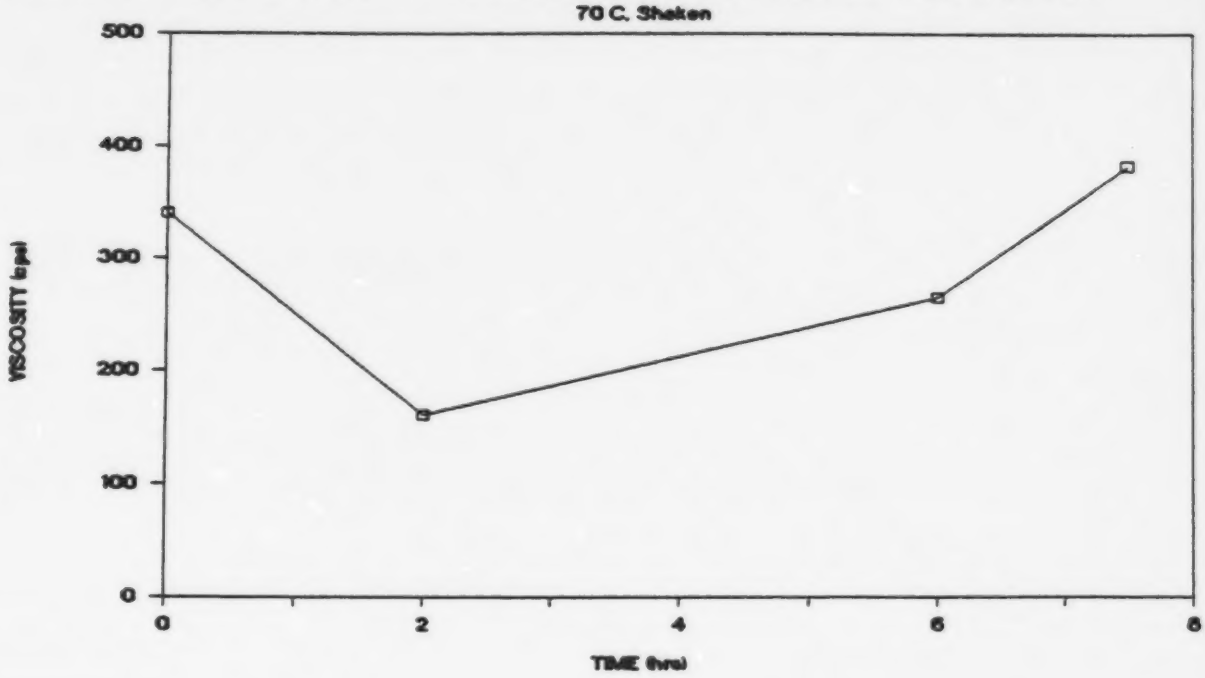


Figure 2-21 LIGNIN/W838 CO-REACTED RESIN GLUE

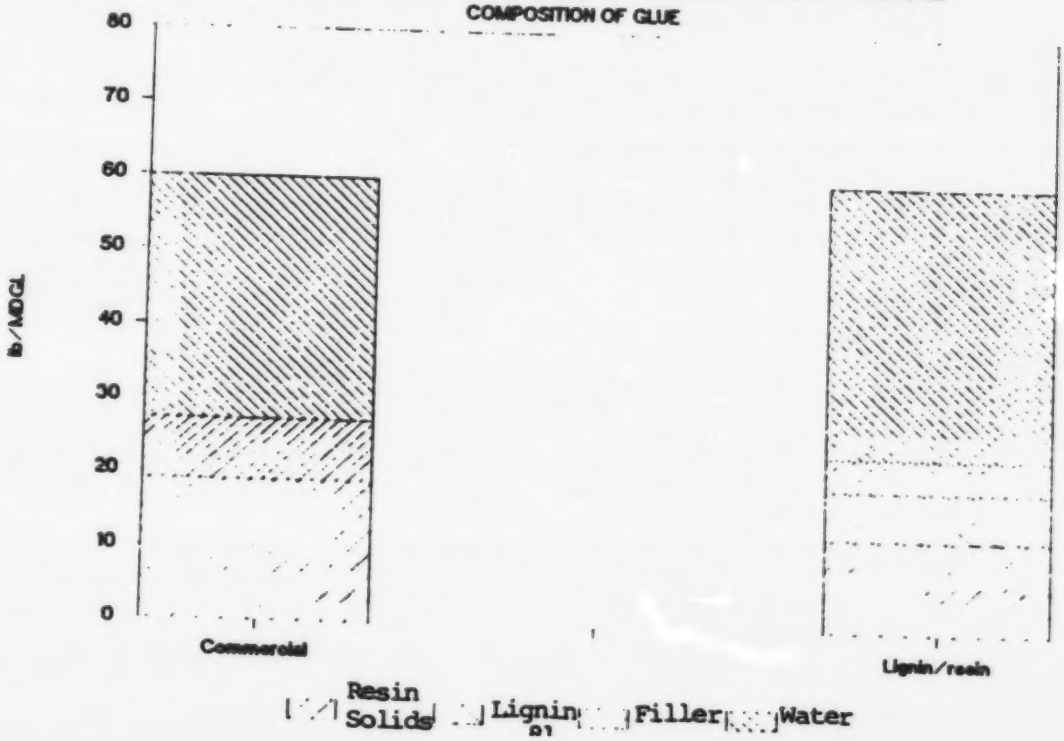


FIGURE 2-22: LIGNIN/W838 RESIN GLUE RESULTS

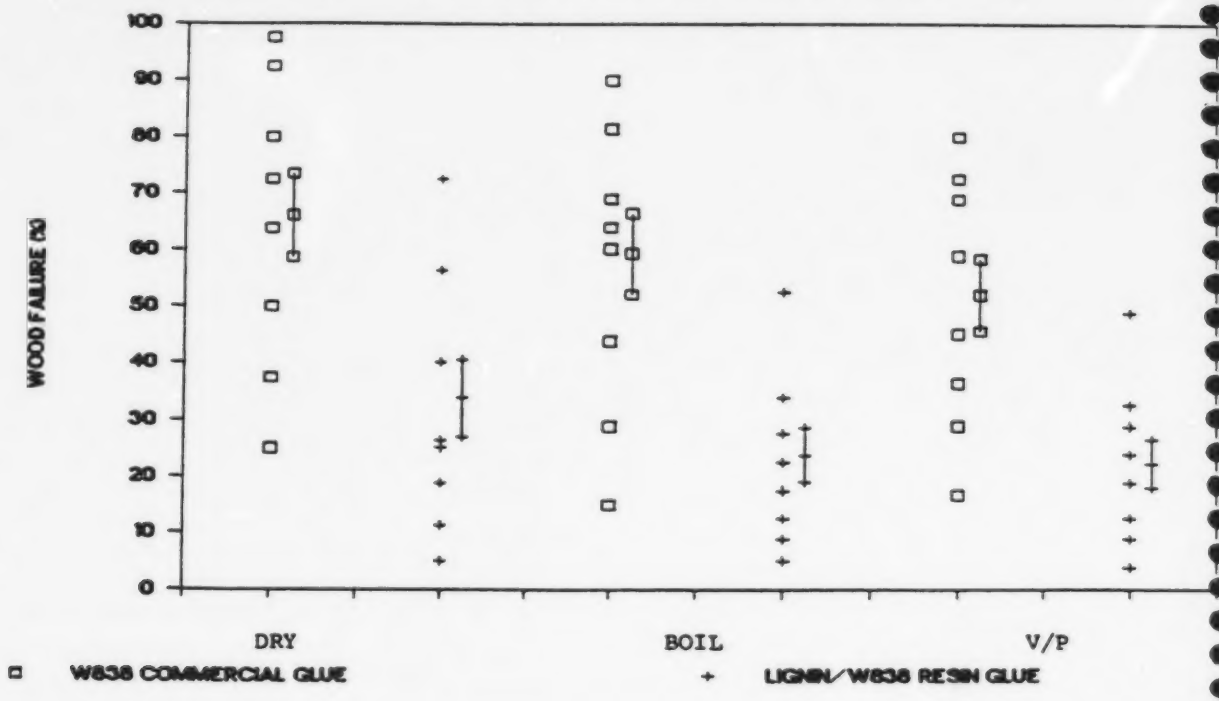


FIGURE 2-23: LIGNIN/W838 RESIN GLUE RESULTS

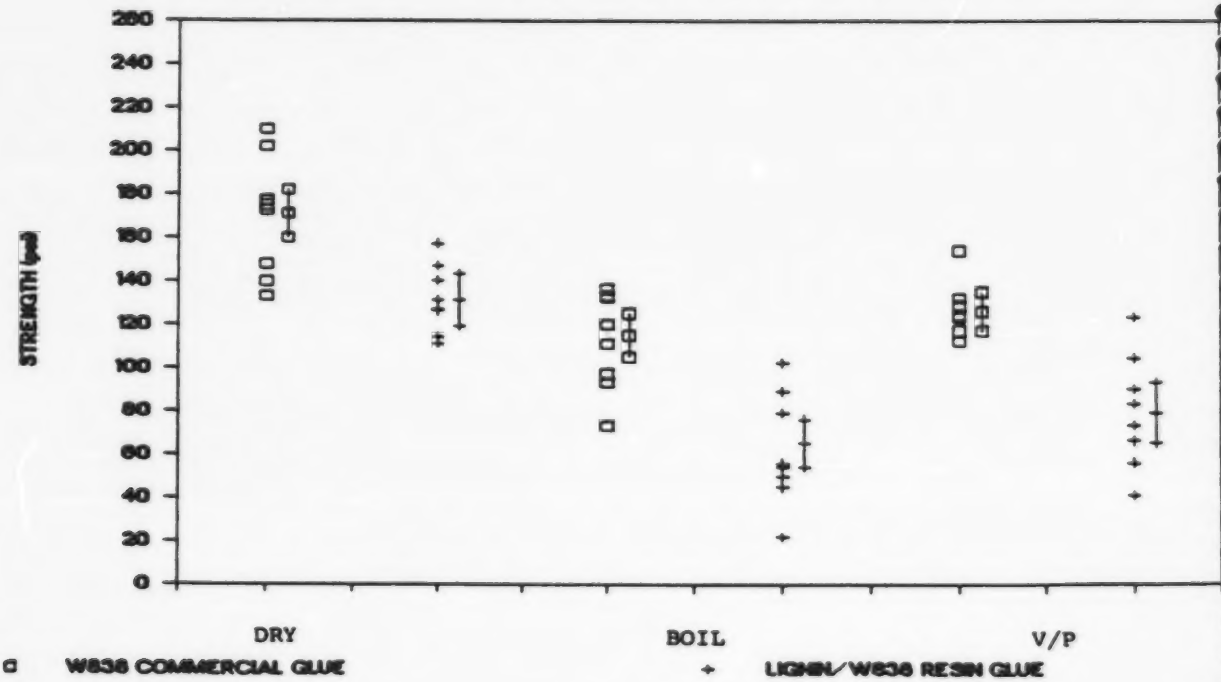
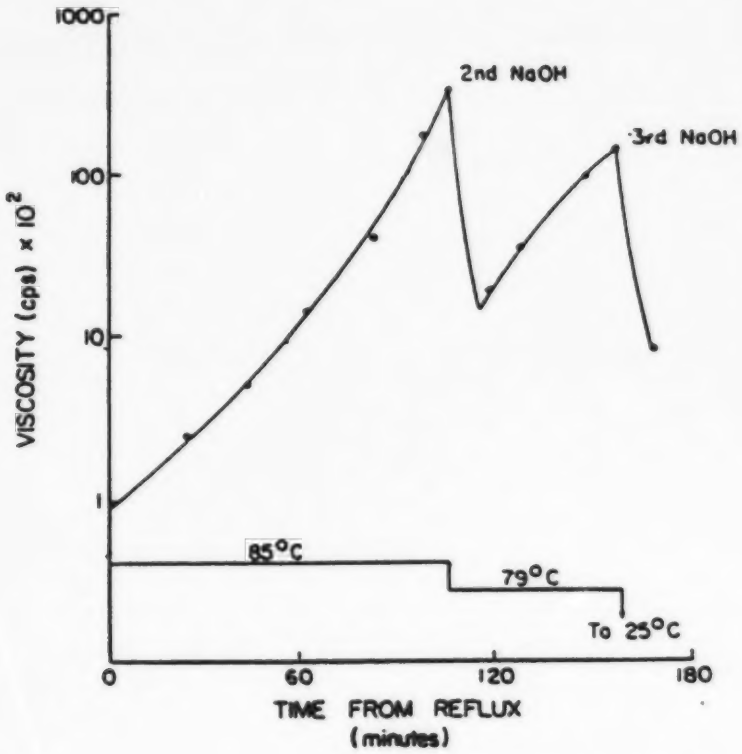


FIGURE 2-24: VISCOSITY PROFILE OF PF RESIN *



* Muller, et.al. (1984)

FIGURE 2-25: TEMPERATURE AND VISCOSITY PROFILE

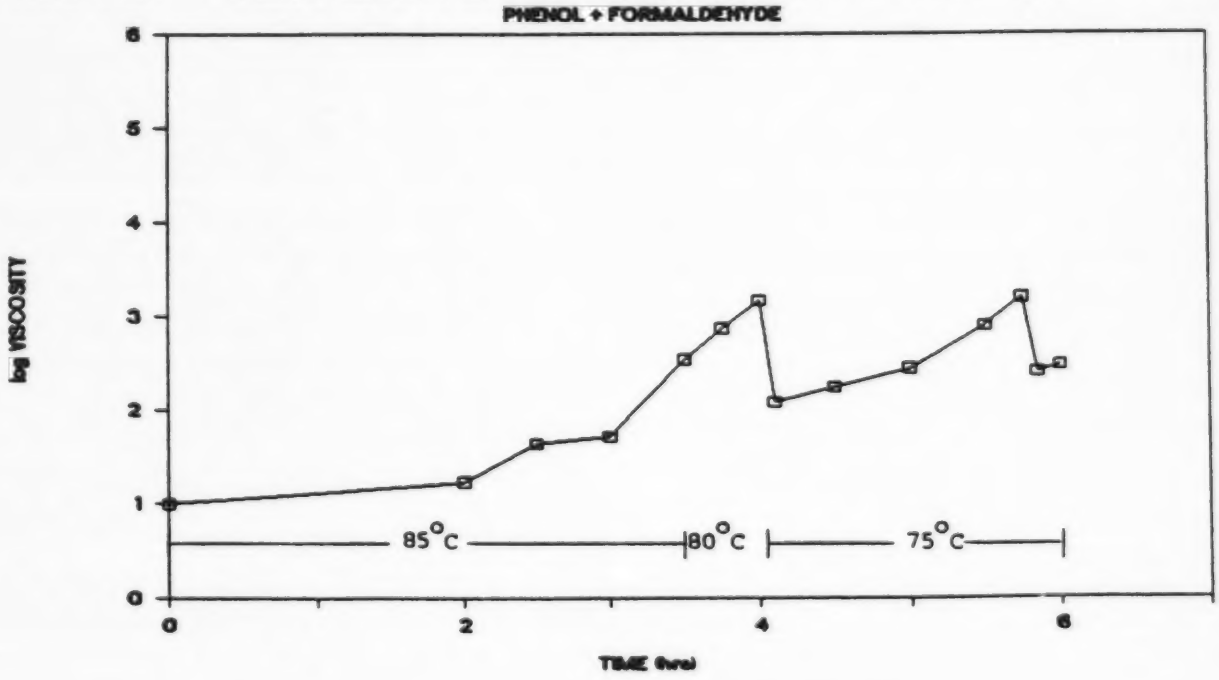


FIGURE 2-26: IOGEN RESIN GLUE RESULTS

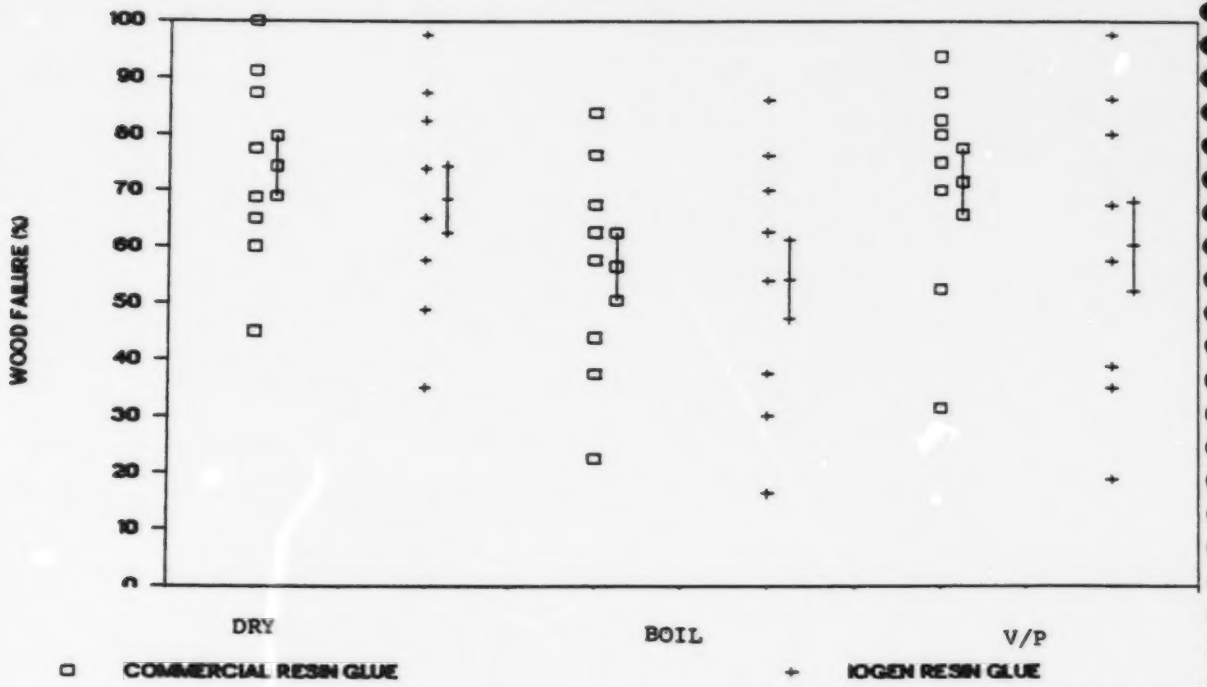


FIGURE 2-27: IOGEN RESIN GLUE RESULTS

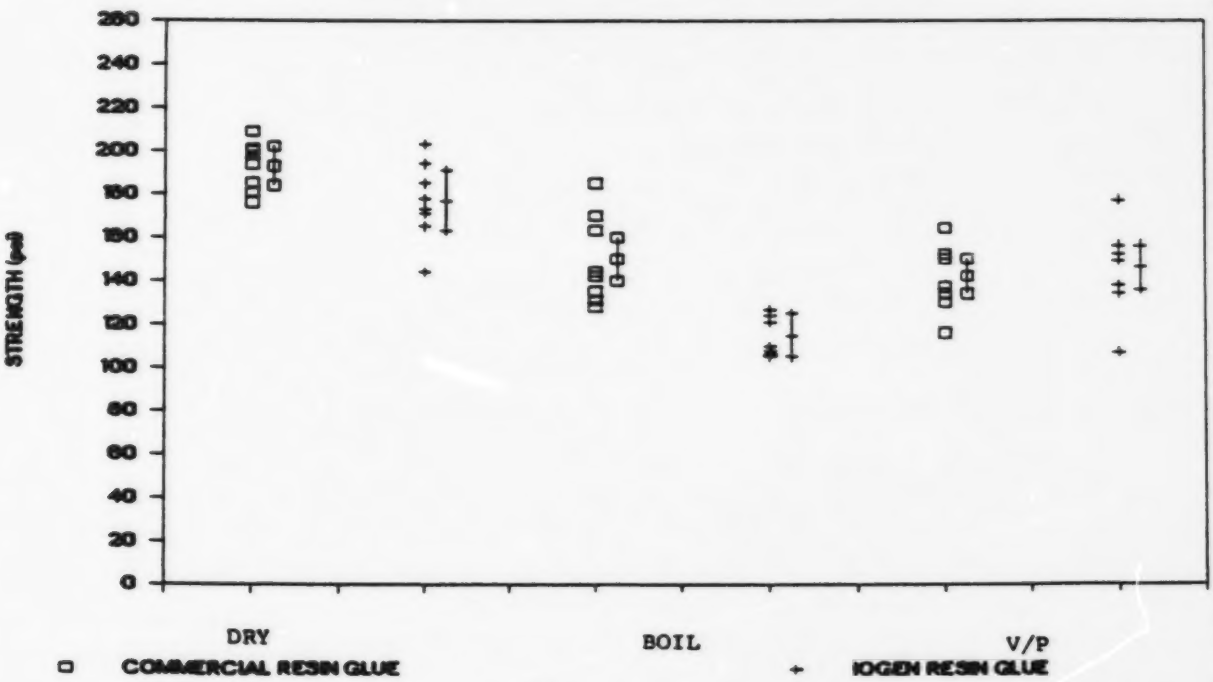


FIGURE 2-28: TEMPERATURE AND VISCOSITY PROFILE

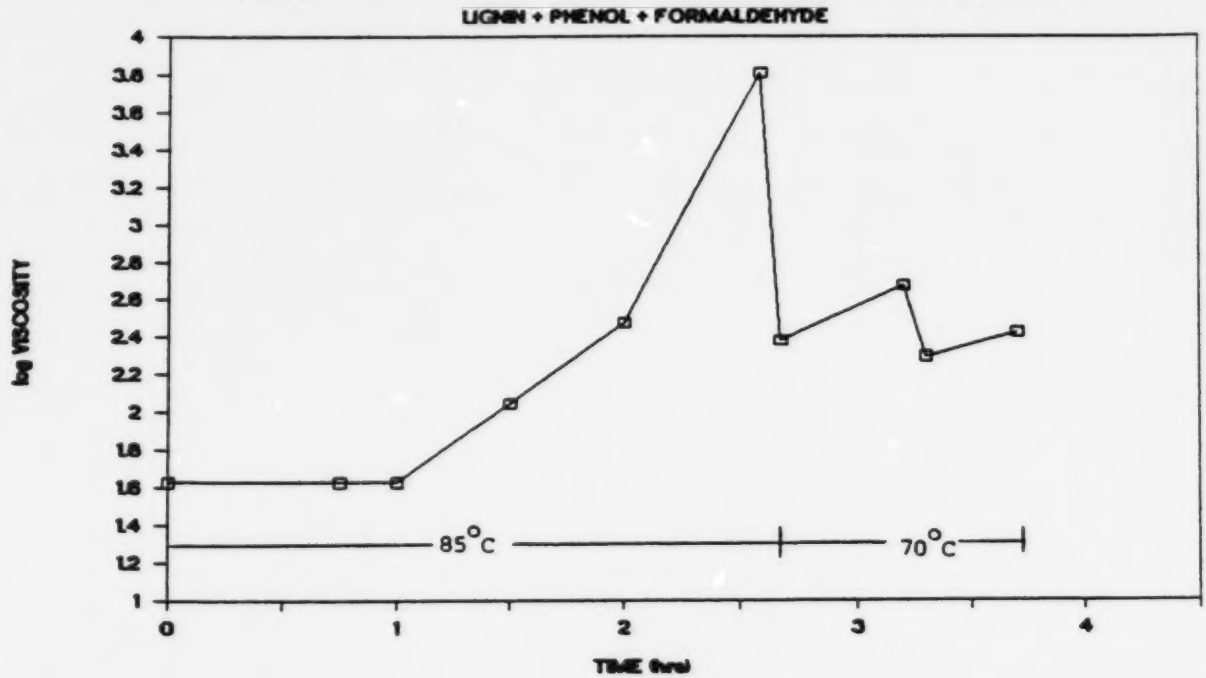


Figure 2-29: LIGNIN PF RESIN GLUE FORMULATION

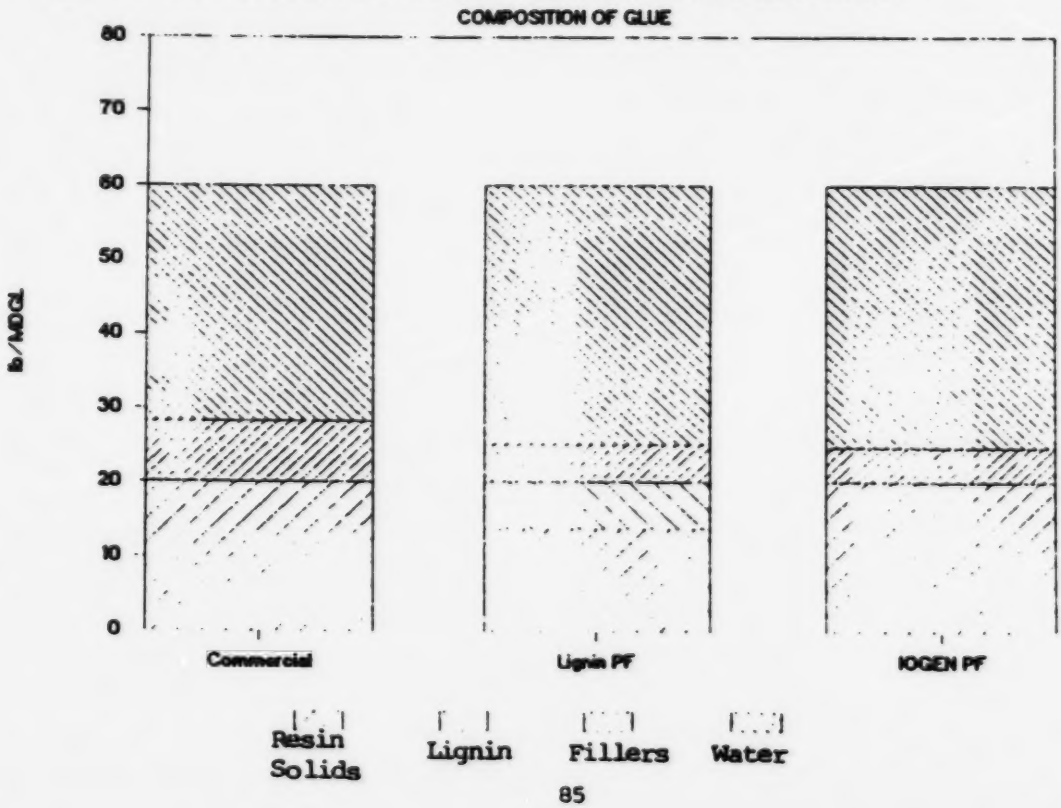


FIGURE 2-30: IOGEN LIGNIN PF GLUE RESULTS

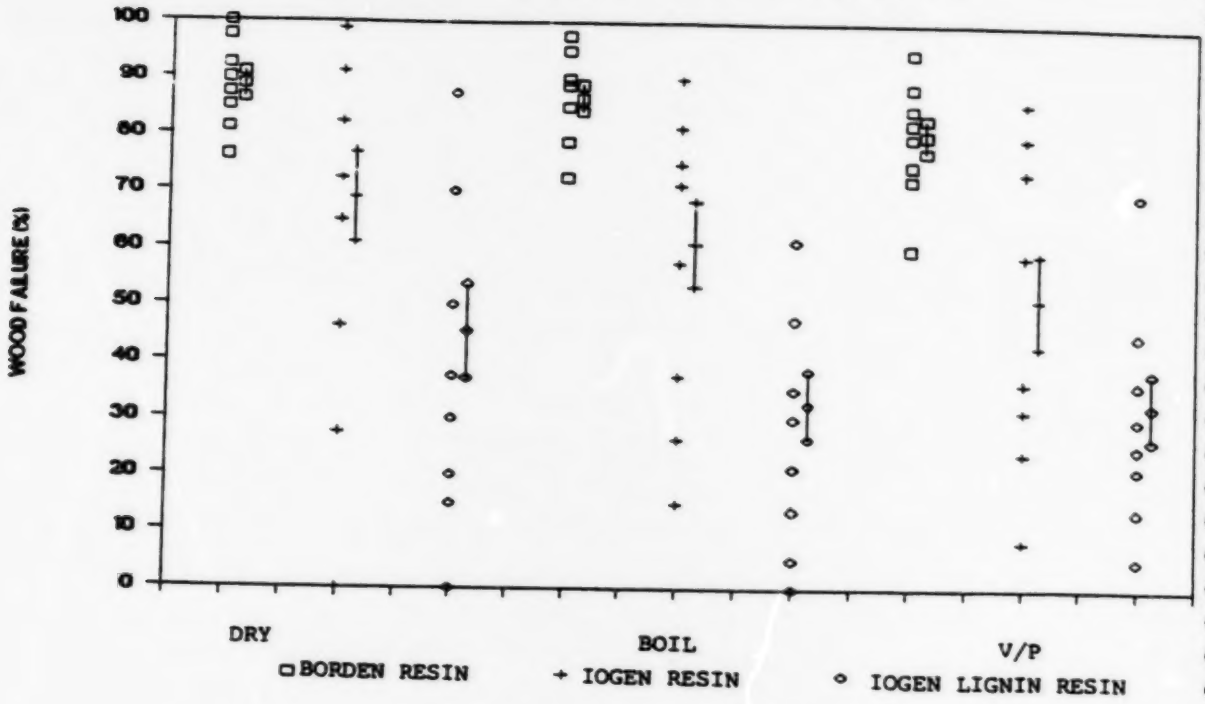


FIGURE 2-31: IOGEN LIGNIN PF GLUE RESULTS

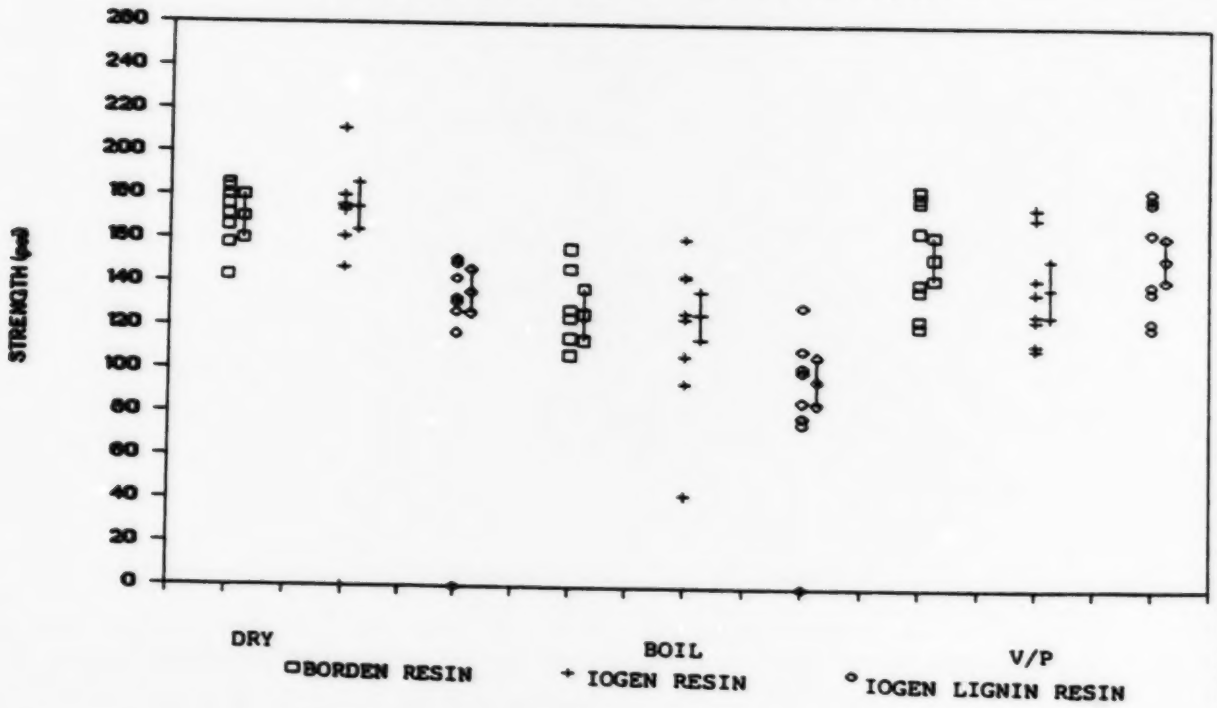


FIGURE 3-1: REACTION OF PHENOL WITH FORMALDEHYDE-FORMATION OF HYDROXYMETHYL PHENOLS (FORSS, 1979)

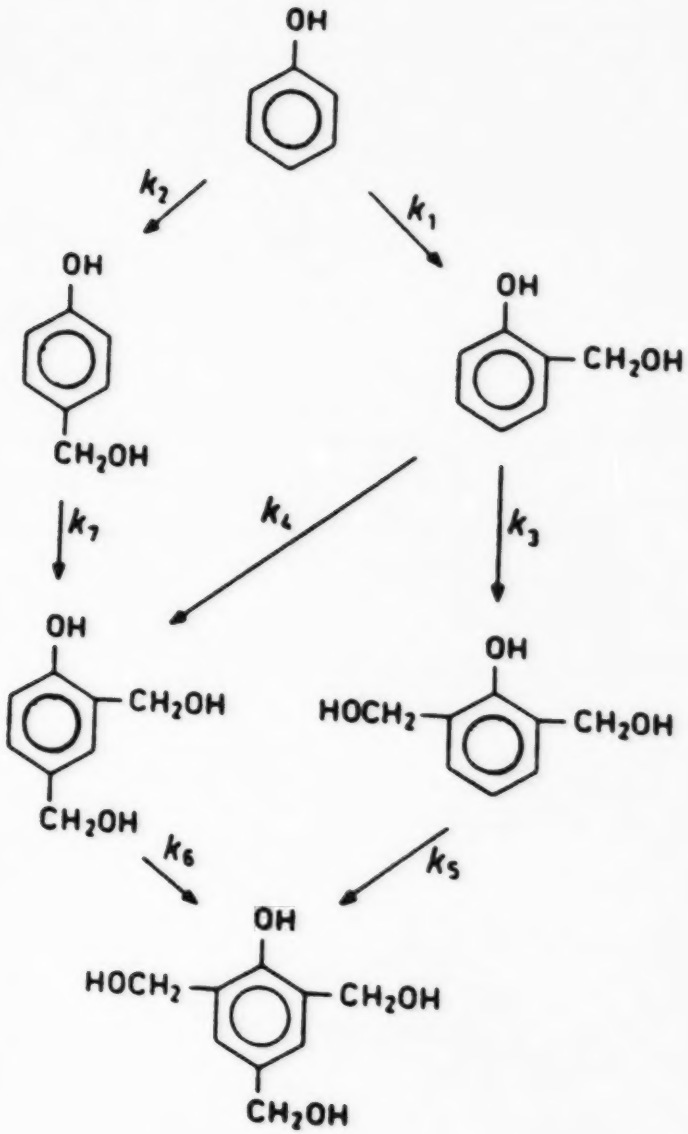
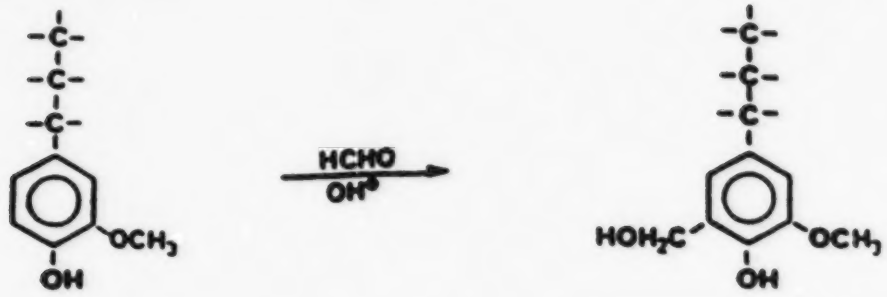
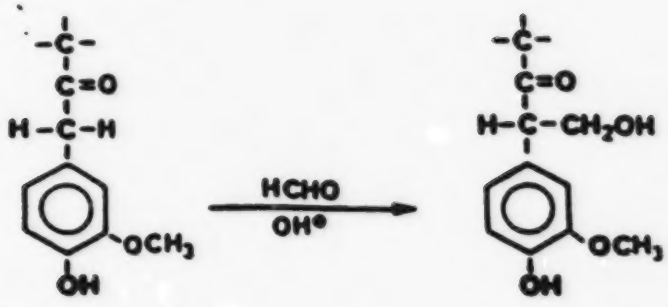


Figure 3-2: REACTION OF LIGNIN WITH FORMALDEHYDE

A. Lederer-Manassa Reaction*



B. Tollen's Reaction*



(* Young, et.al , 1985)

FIGURE 3-3:

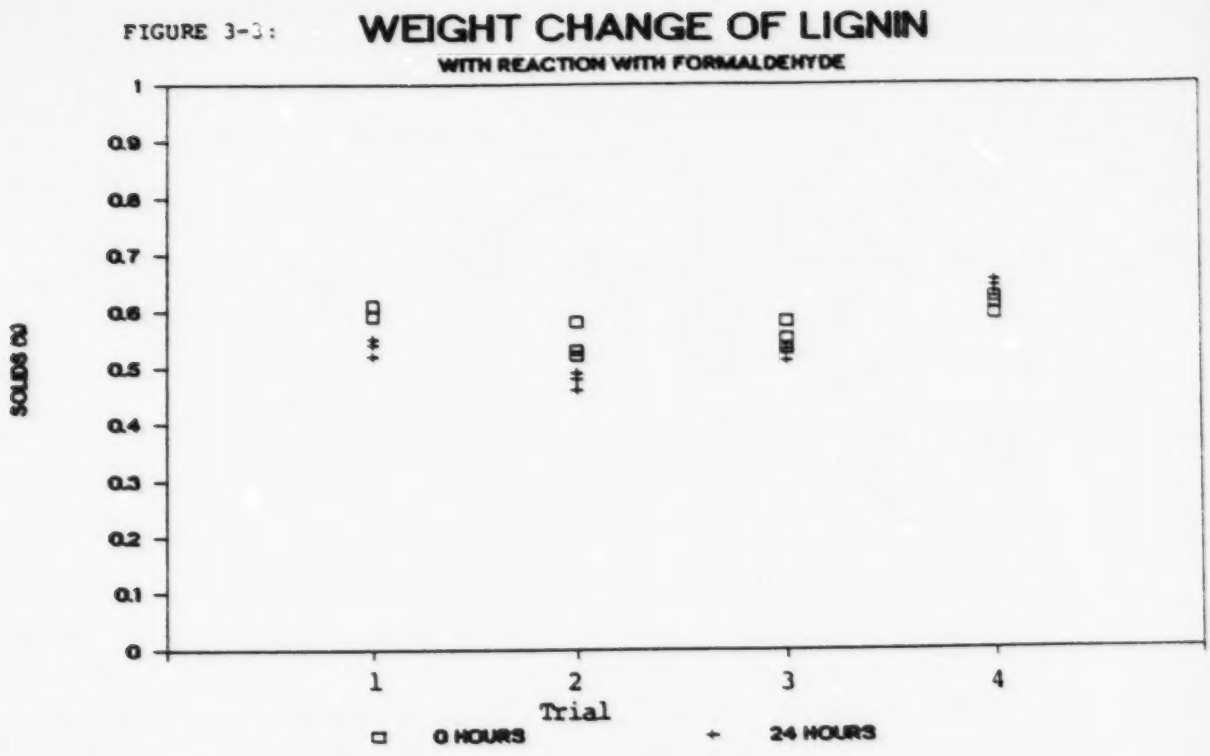


FIGURE 3-4:

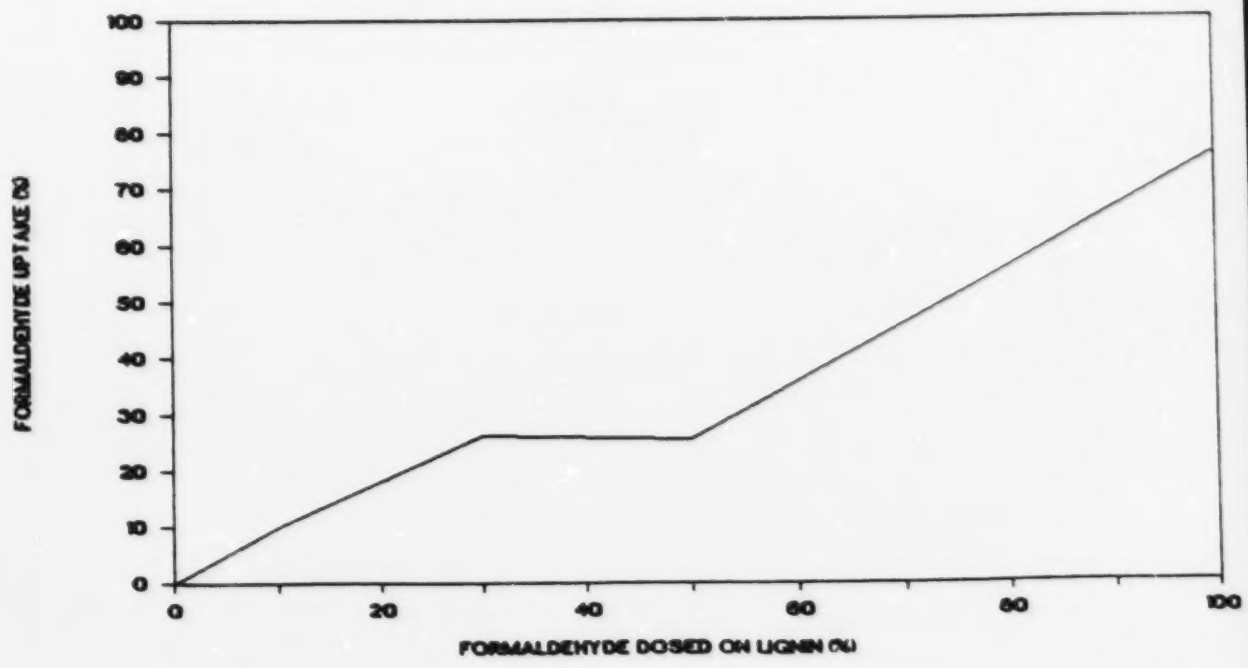
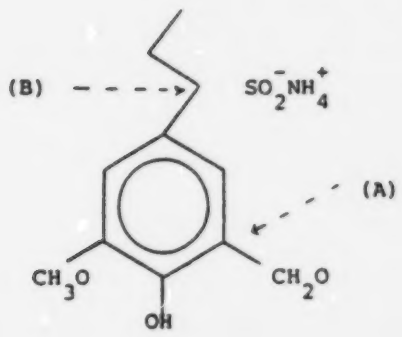


FIGURE 3-5: PHENOLATION OF AMMONIUM LIGNOSULFONATE



Sites of Phenolation

(A) Muller and Glasser (1984)
(B) Kratzl and Oburger (1980)

FIGURE 3-6: REACTIVITY OF PHENOLATED LIGNIN WITH FORMALDEHYDE

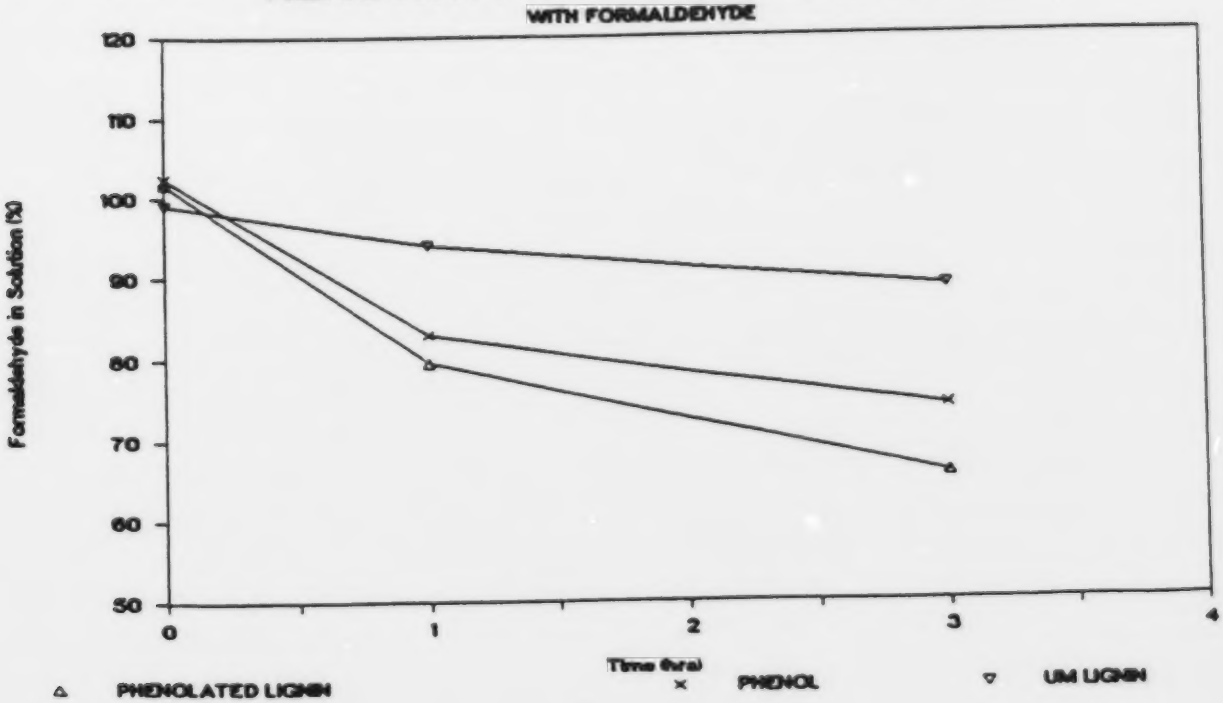
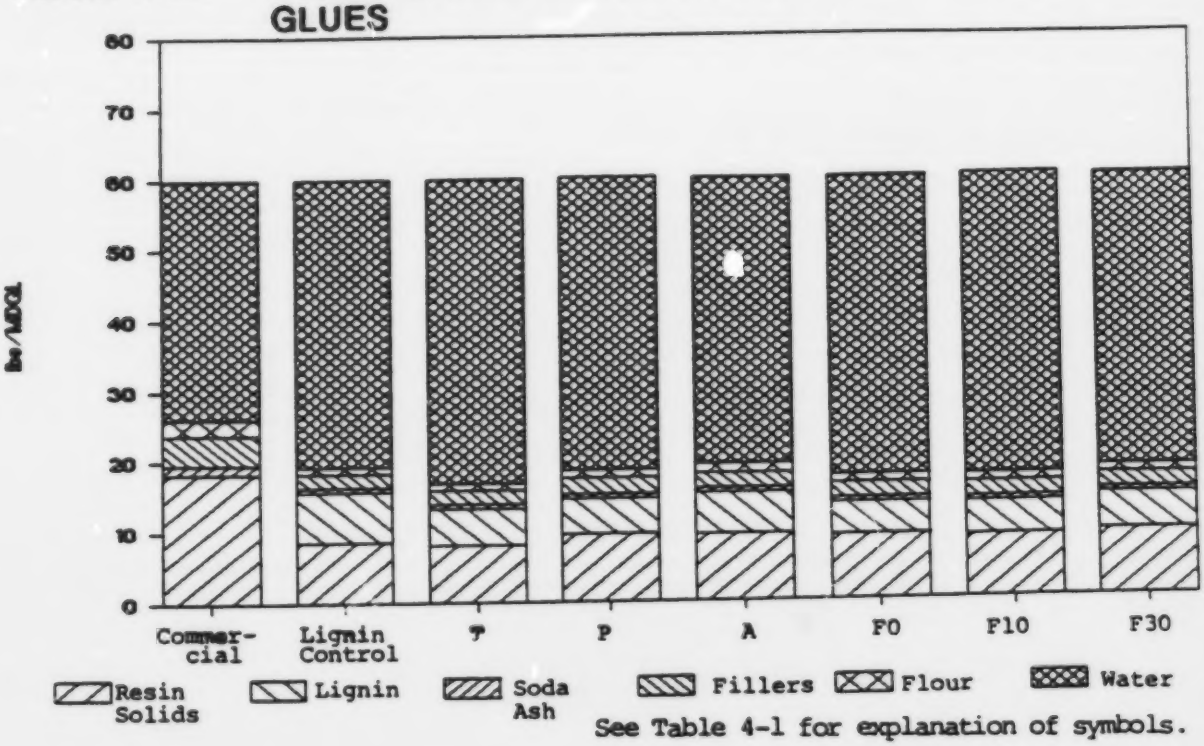
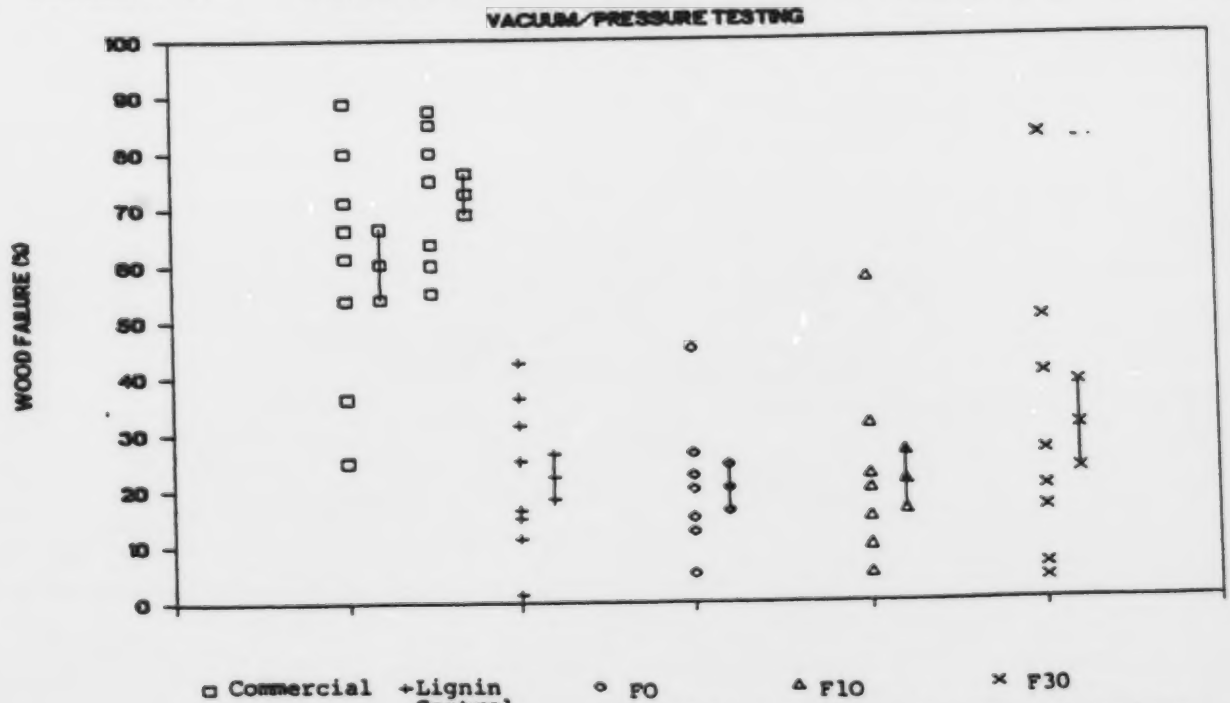


FIGURE 4-1: COMPOSITION OF HYDROXYMETHYLATED LIGNIN GLUES



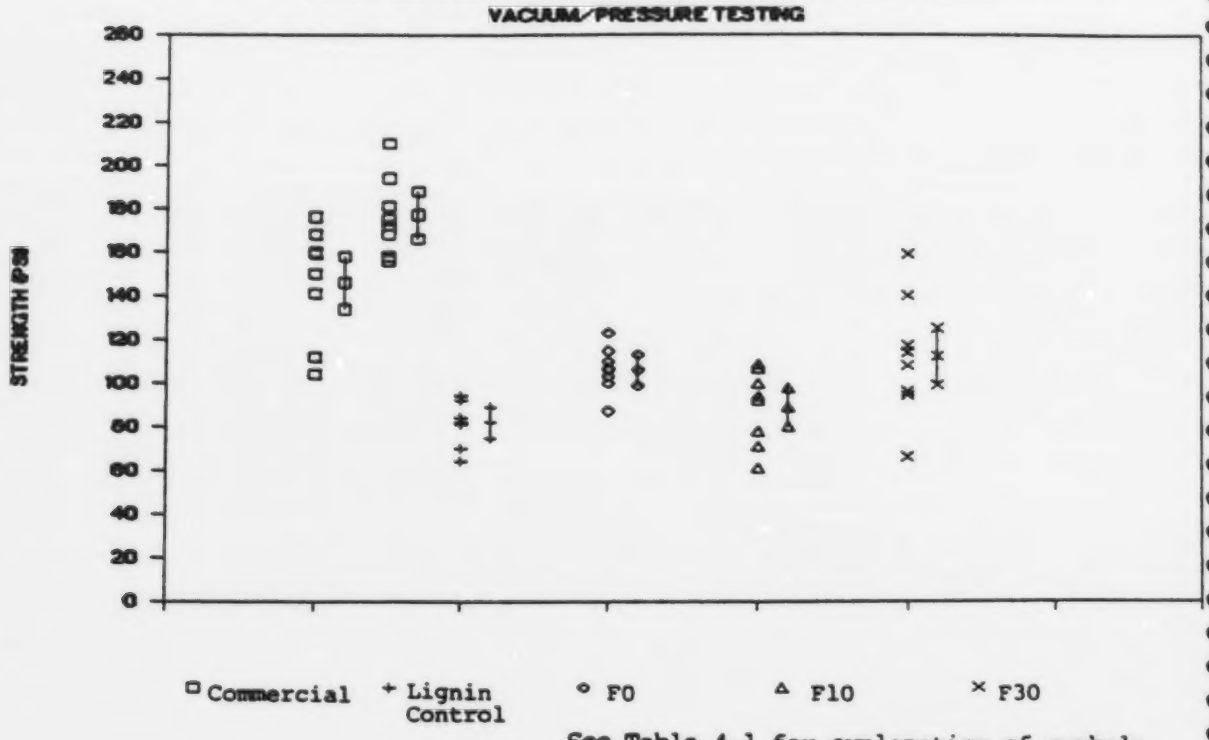
See Table 4-1 for explanation of symbols.

FIGURE 4-2: WOOD FAILURE RESULTS FOR HM LIGNIN GLUES



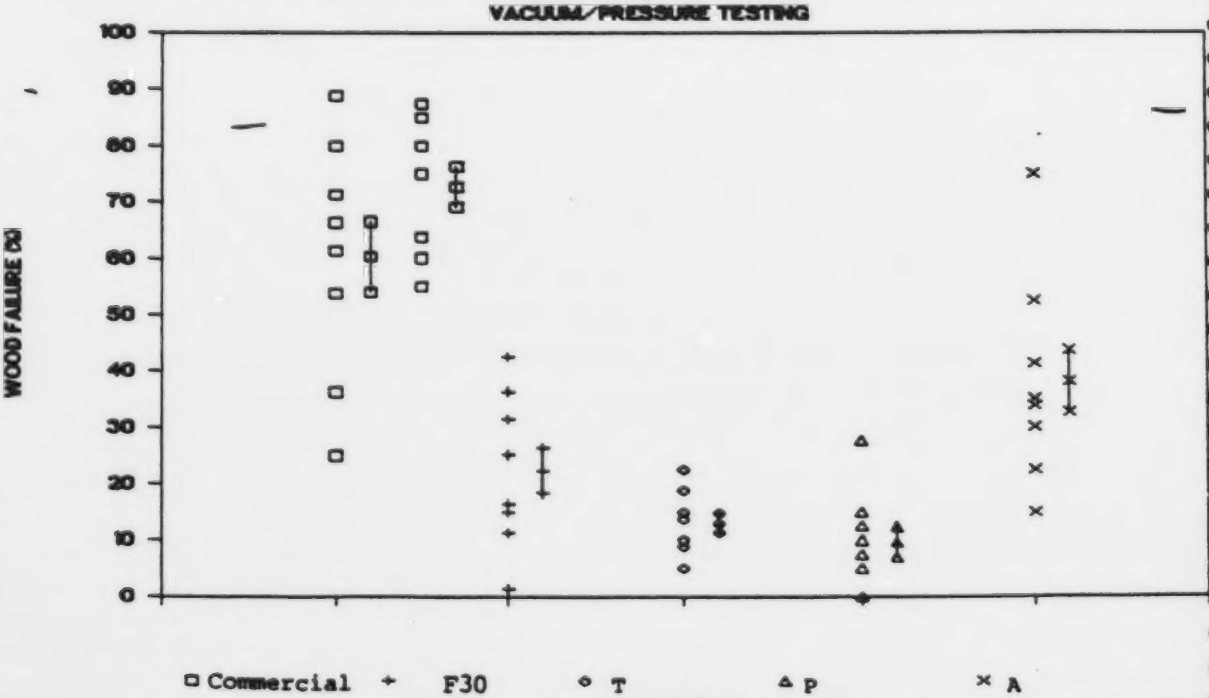
See Table 4-1 for explanation of symbols.

FIGURE 4-3: VARYING FORMALDEHYDE LEVELS



See Table 4-1 for explanation of symbols.

Figure 4-4: EFFECT OF TEMP., pH, AND AERATION



See Table 4-1 for explanation of symbols

FIGURE 4-5: EFFECT OF TEMP., pH, AND AERATION

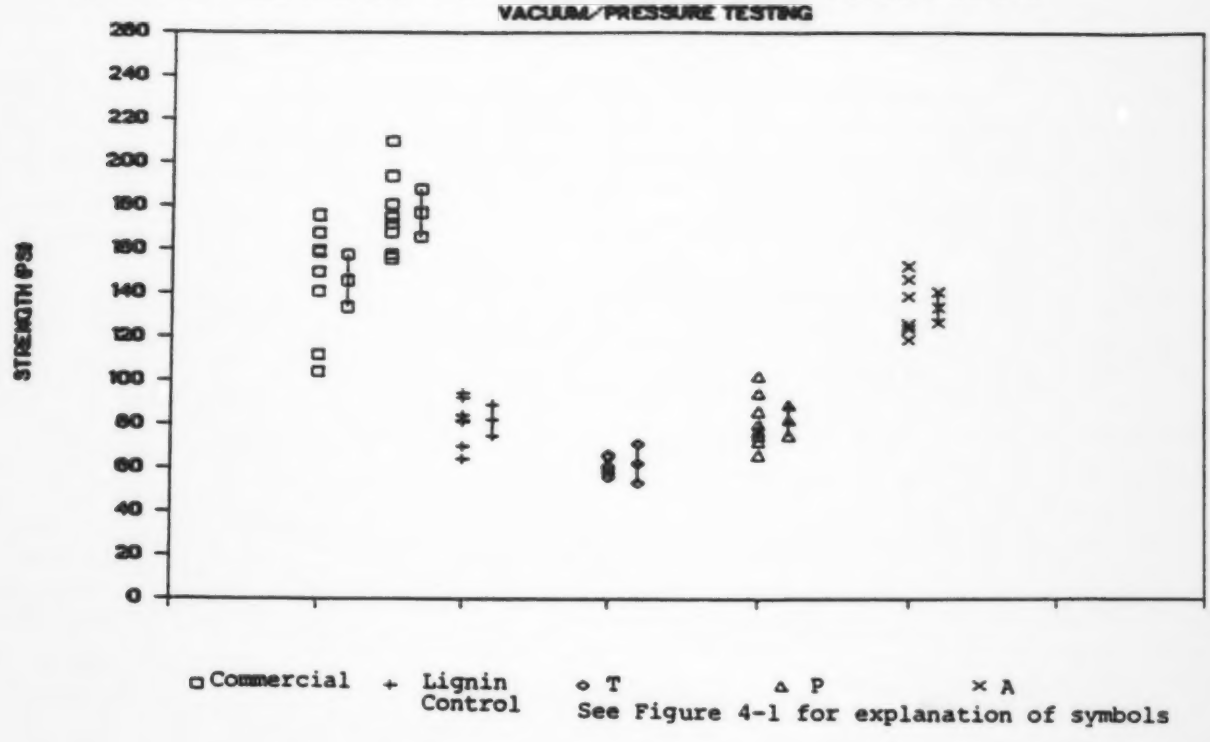


FIGURE 4-6: TEMPERATURE AND VISCOSITY PROFILE

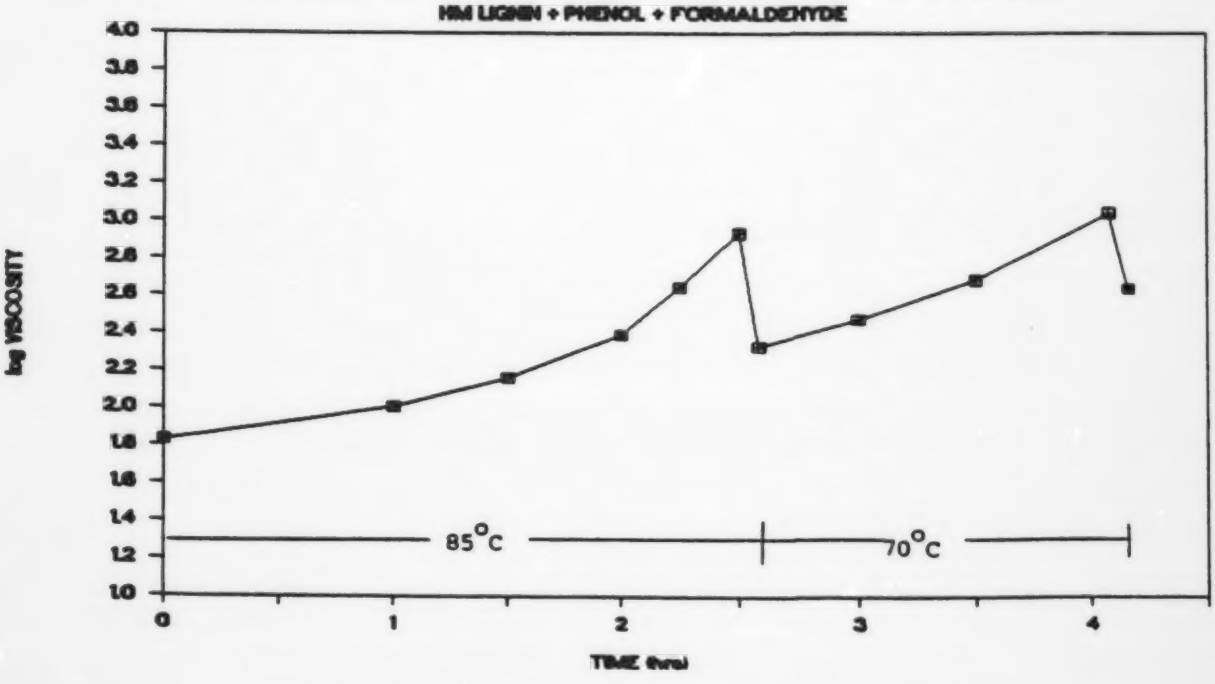


FIGURE 4-7: HM LIGNIN PF PLYWOOD GLUE

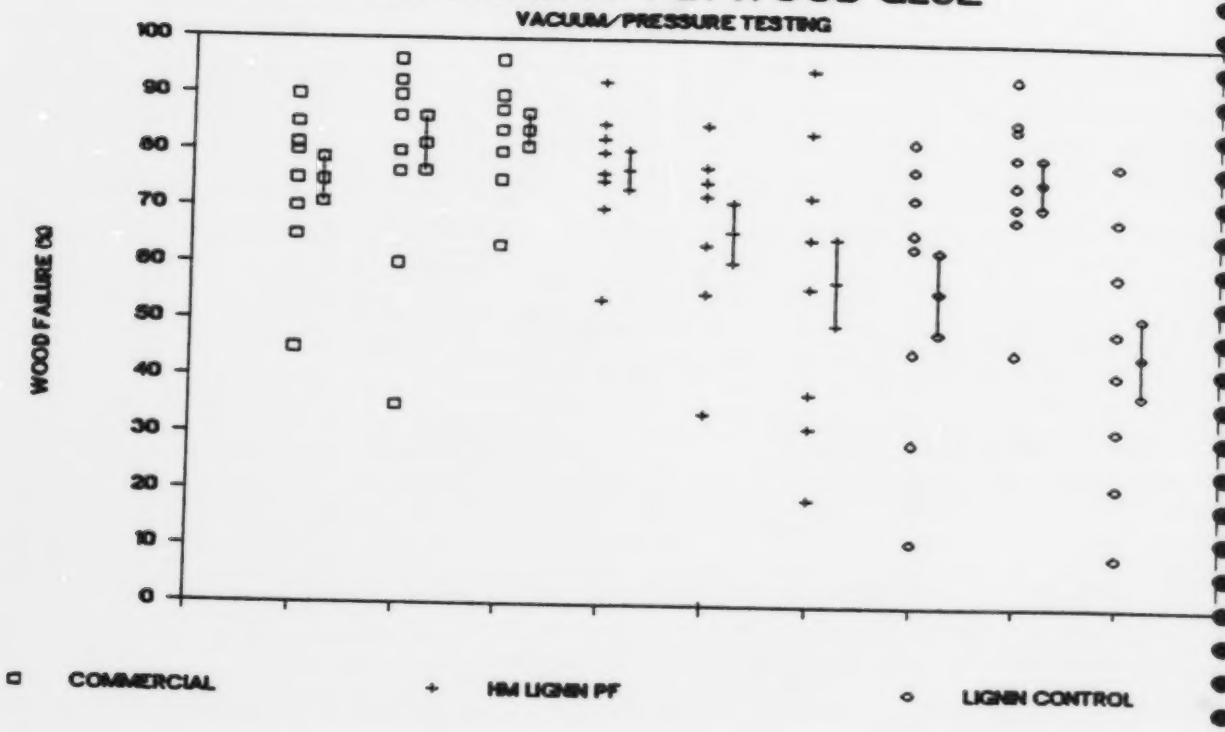


FIGURE 4-8: HM LIGNIN PF PLYWOOD GLUE

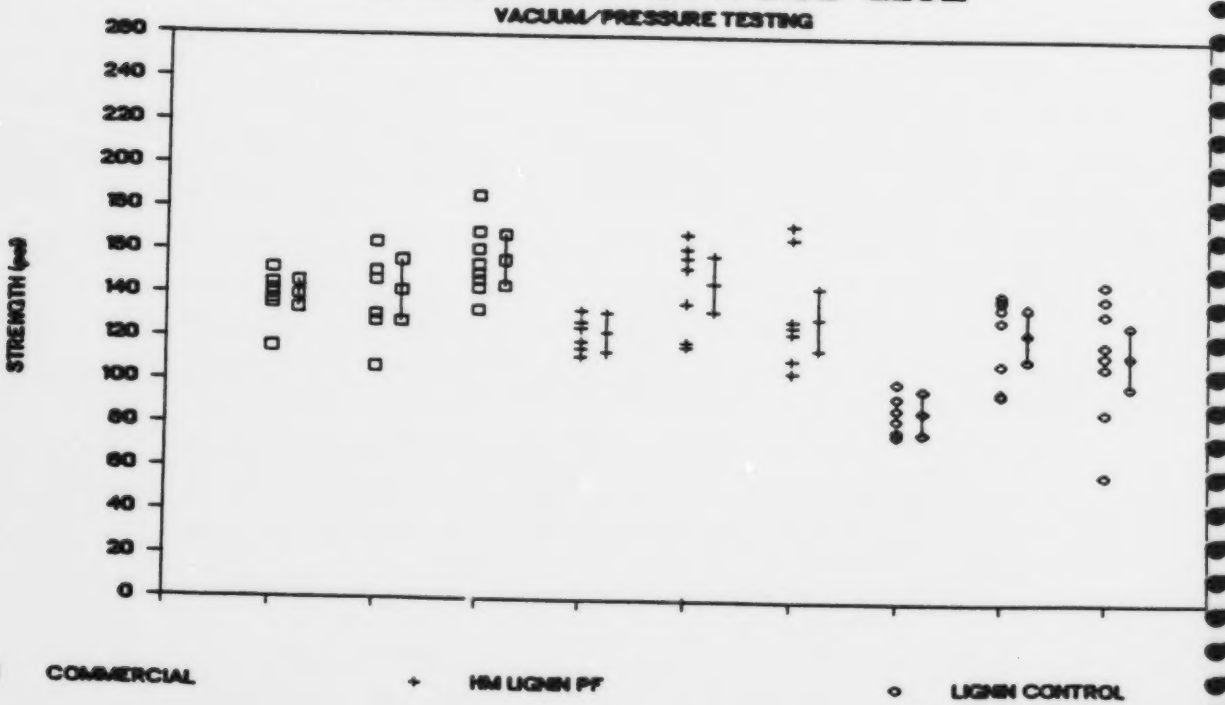


FIGURE 4-11: PHENOLATED LIGNIN WOOD FAILURE IN PLYWOOD GLUE

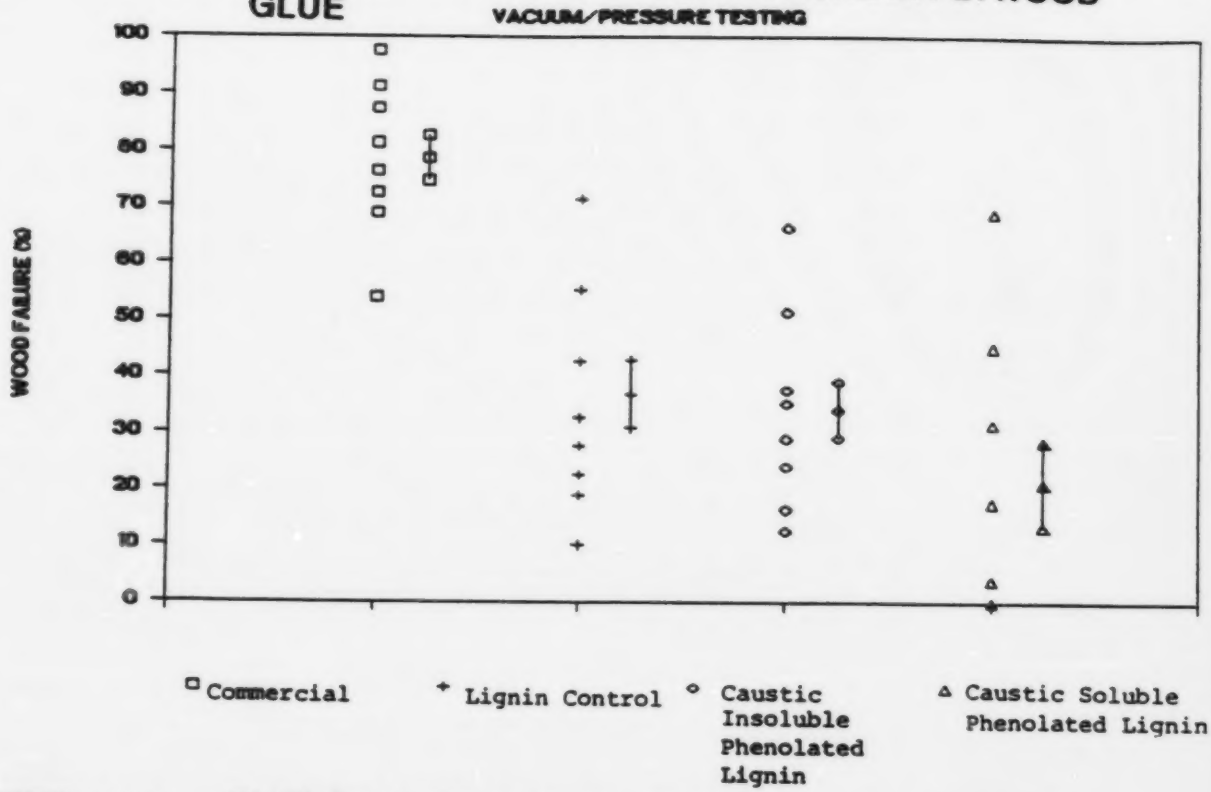


FIGURE 4-12: PHENOLATED LIGNIN STRENGTH IN PLYWOOD GLUE

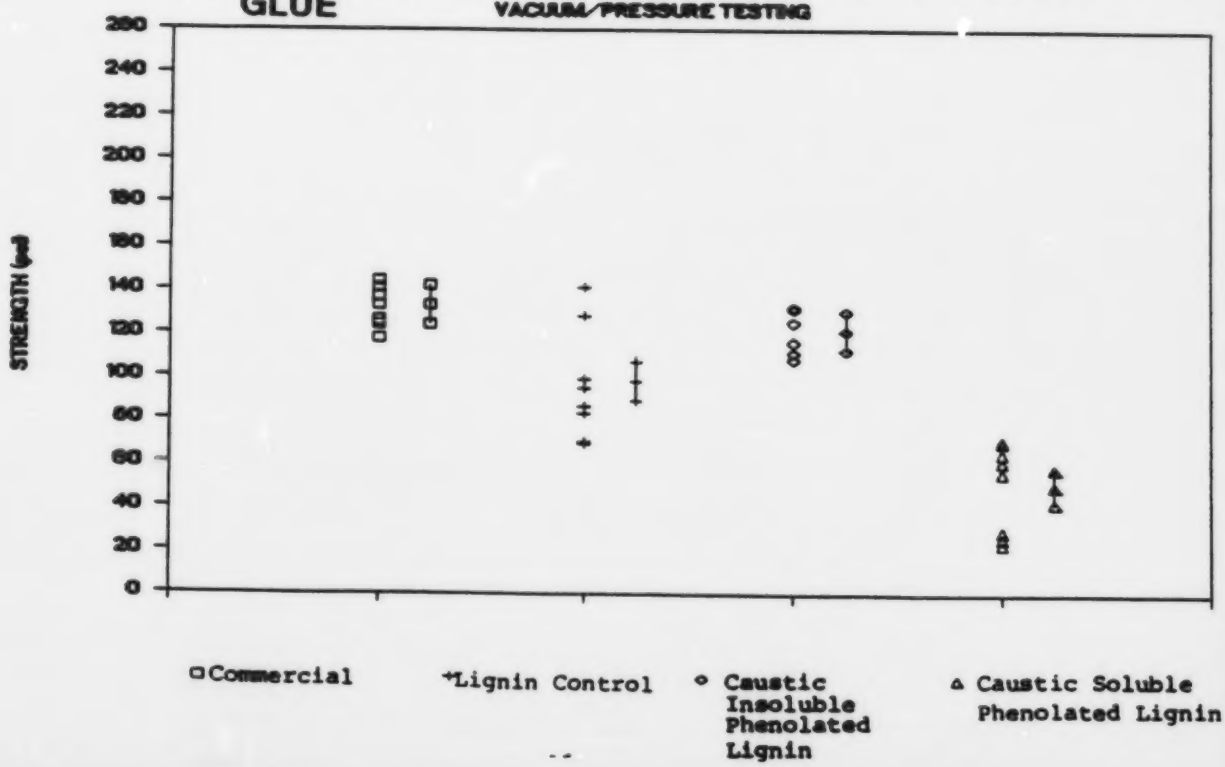


FIGURE 4-11: PHENOLATED LIGNIN WOOD FAILURE IN PLYWOOD GLUE

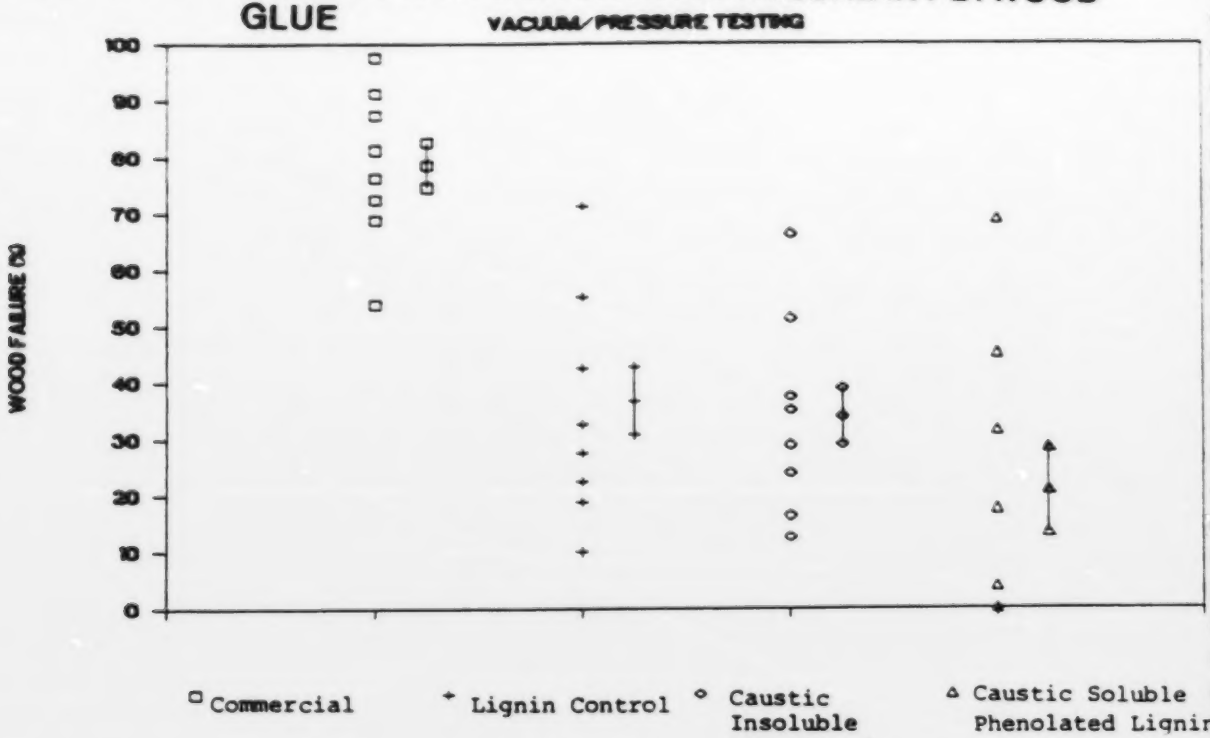


FIGURE 4-12: PHENOLATED LIGNIN STRENGTH IN PLYWOOD GLUE

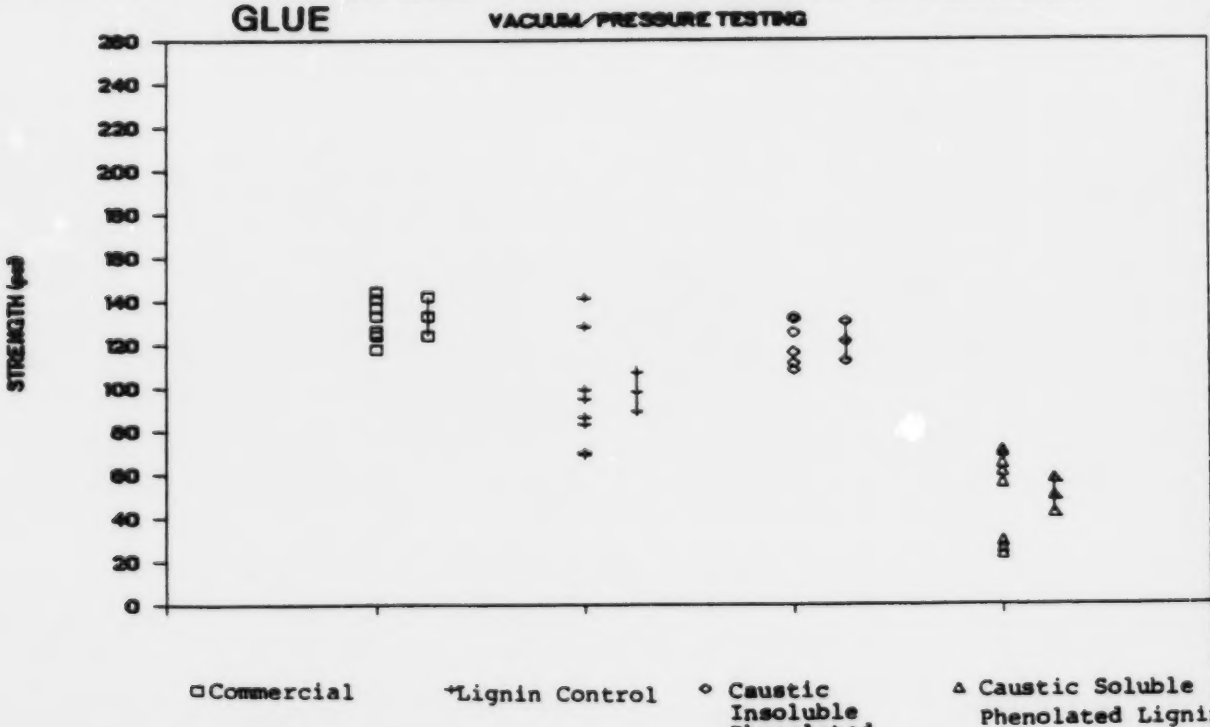


FIGURE 4-13:

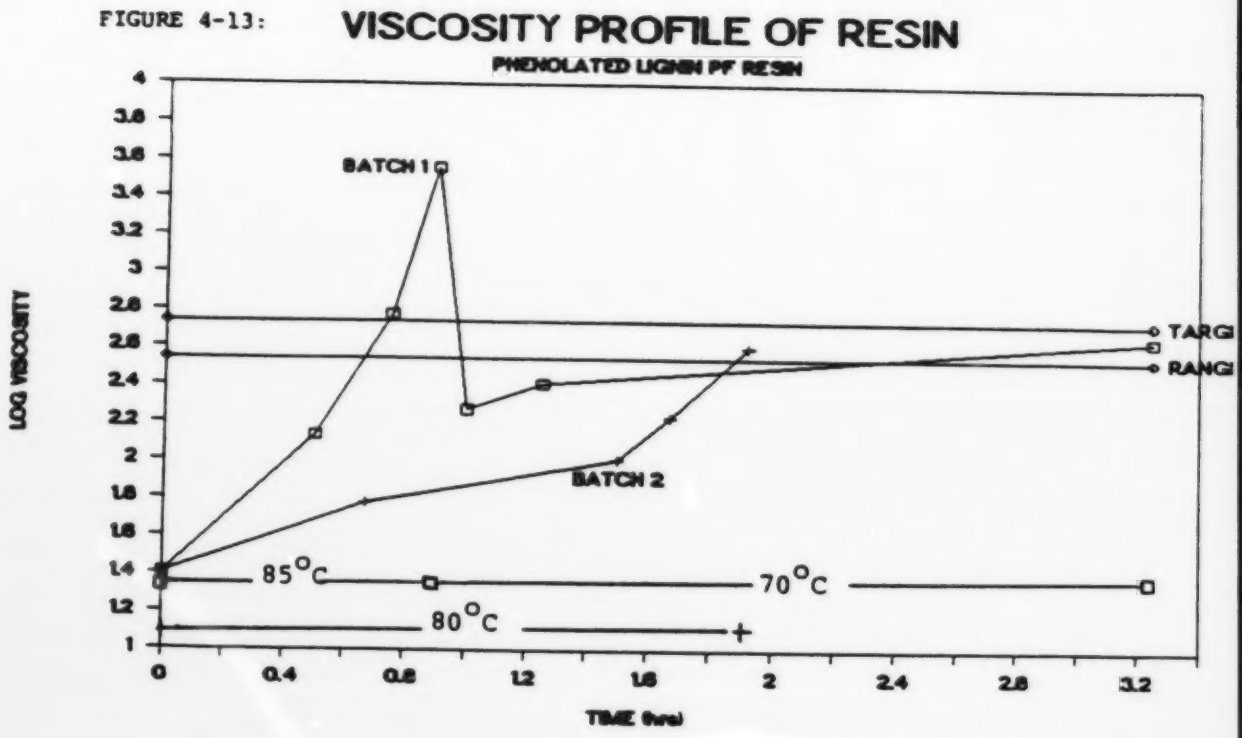

VISCOSITY PROFILE OF RESIN
PHENOLATED LIGNIN PF RESIN
LOG VISCOSITY
TIME (hrs)
BATCH 1
BATCH 2
85°C
70°C
80°C
TARGE
RANGE
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2

Figure 4-14: PHENOLATED LIGNIN PF RESIN GLUES

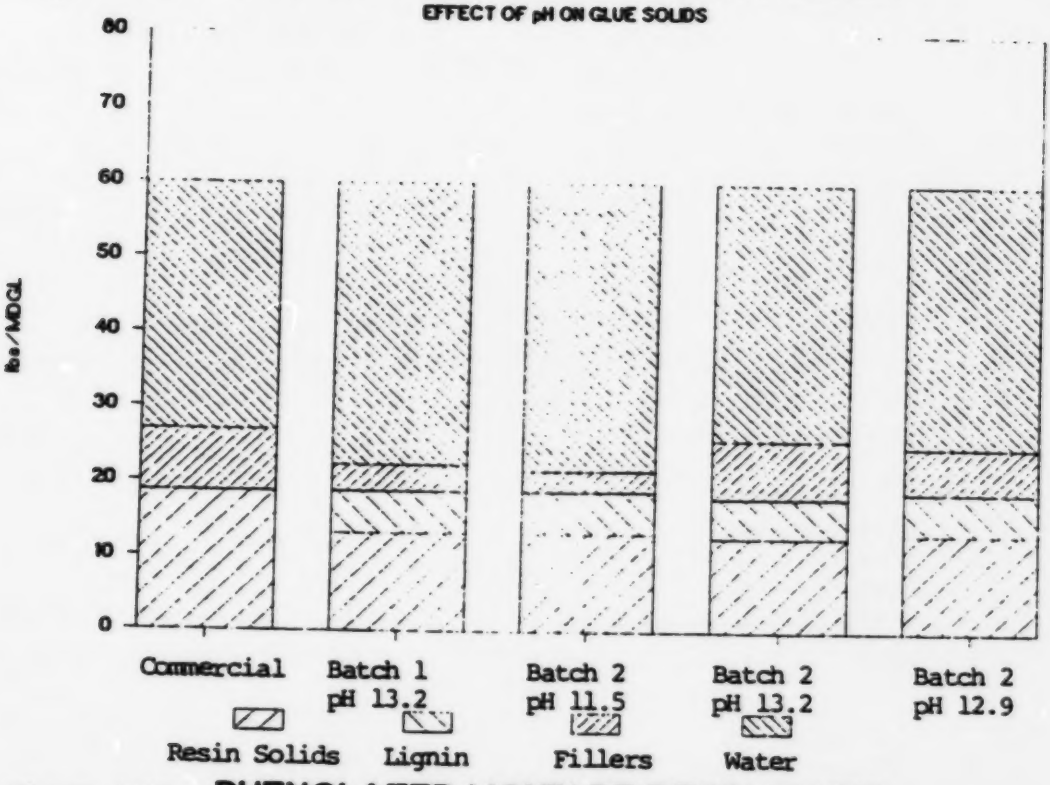


Figure 4-15: PHENOLATED LIGNIN PF RESIN GLUES

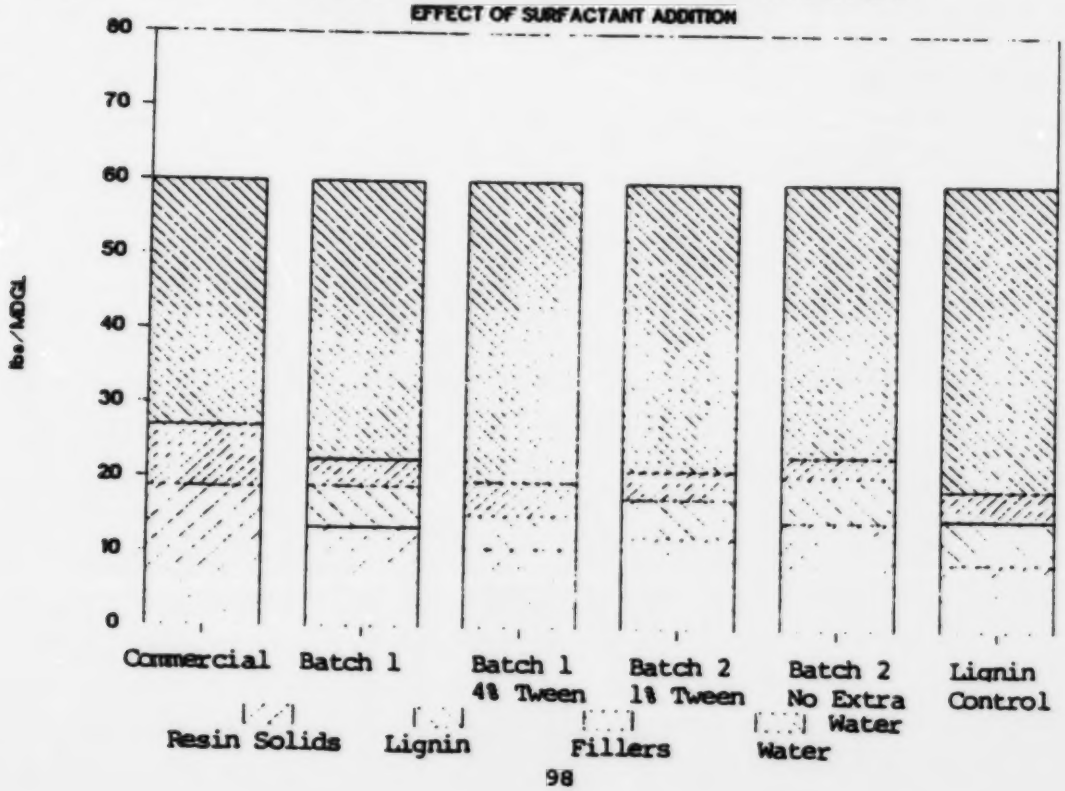


FIGURE 4-16: PHENOLATED LIGNIN PF RESIN GLUE

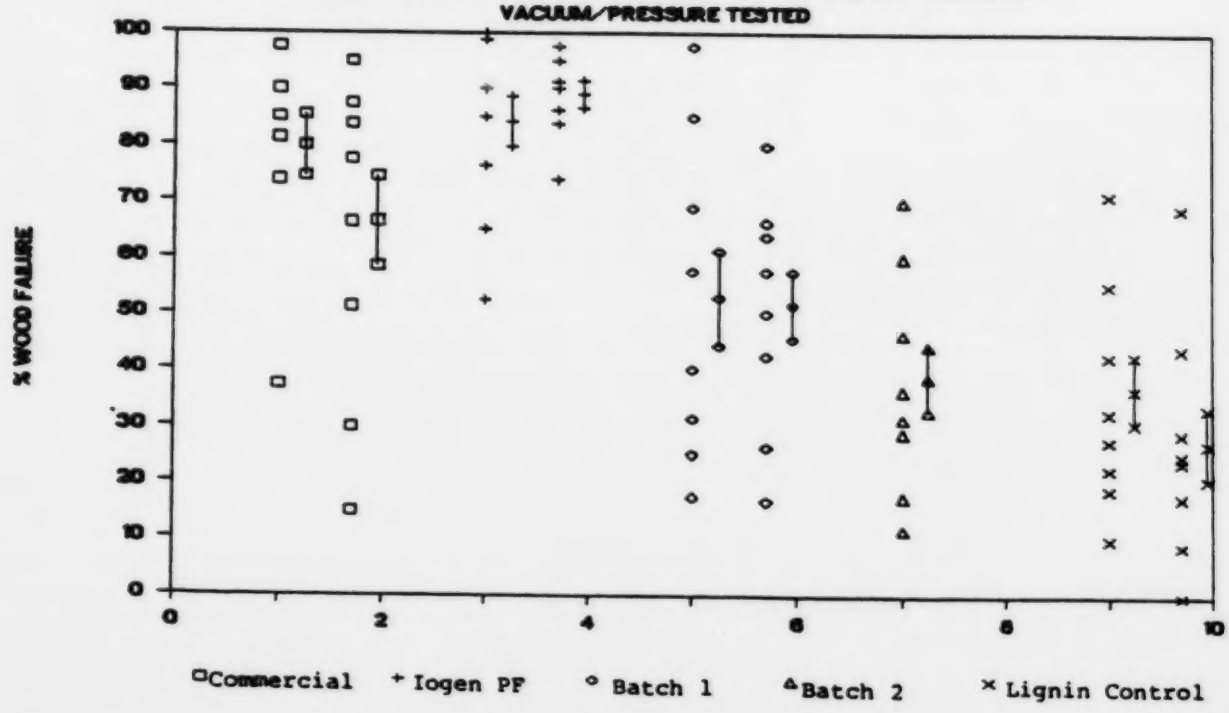


FIGURE 4-17: PHENOLATED LIGNIN GLUE RESULTS

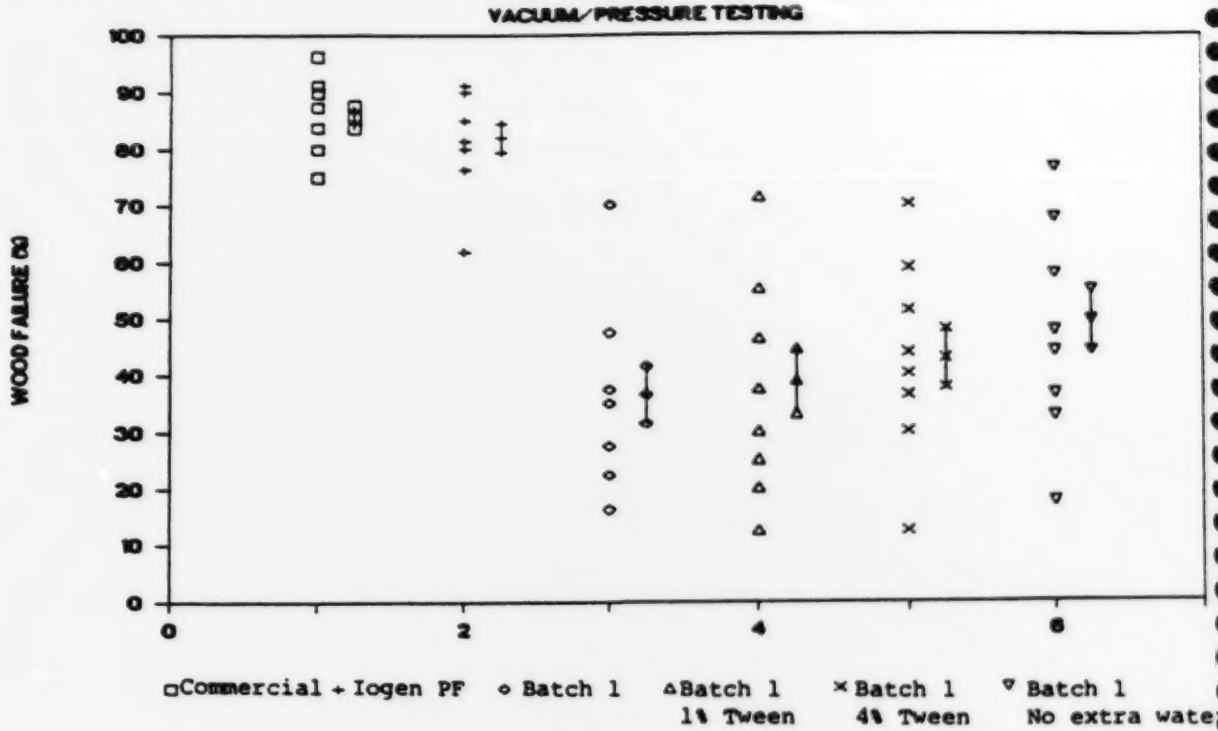


FIGURE 4-18: PHENOLATED LIGNIN PF RESIN GLUE

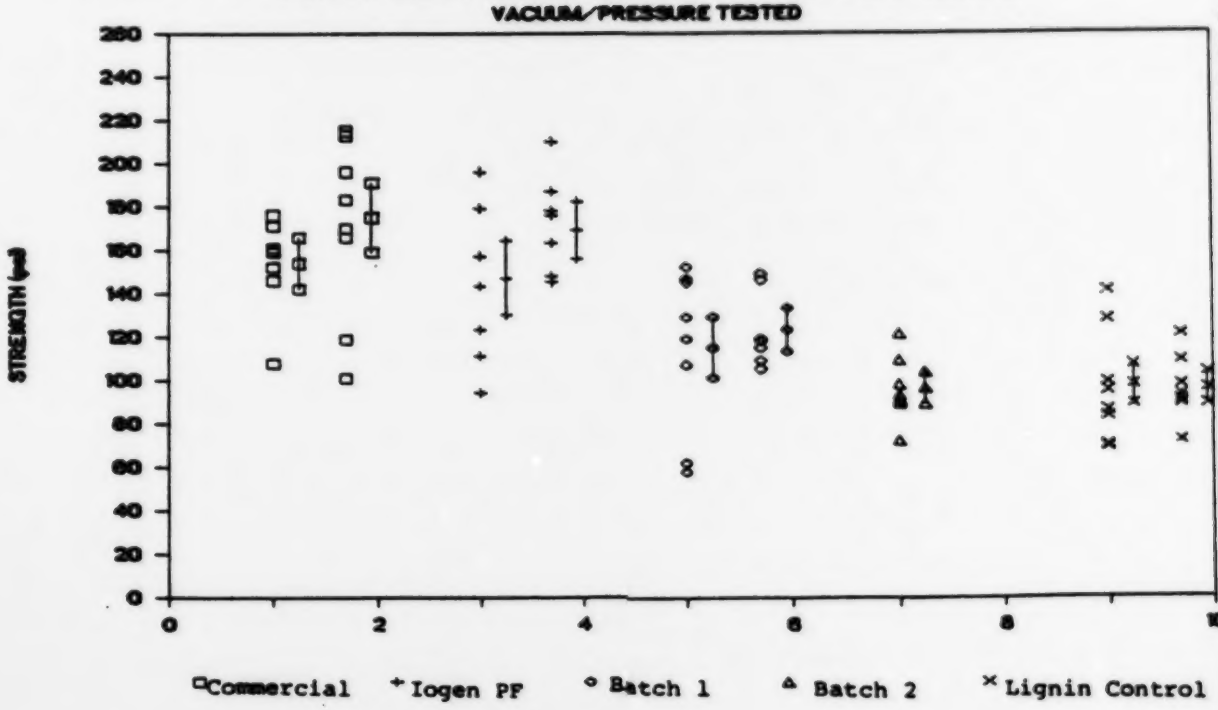


FIGURE 4-19: PHENOLATED LIGNIN GLUE RESULTS

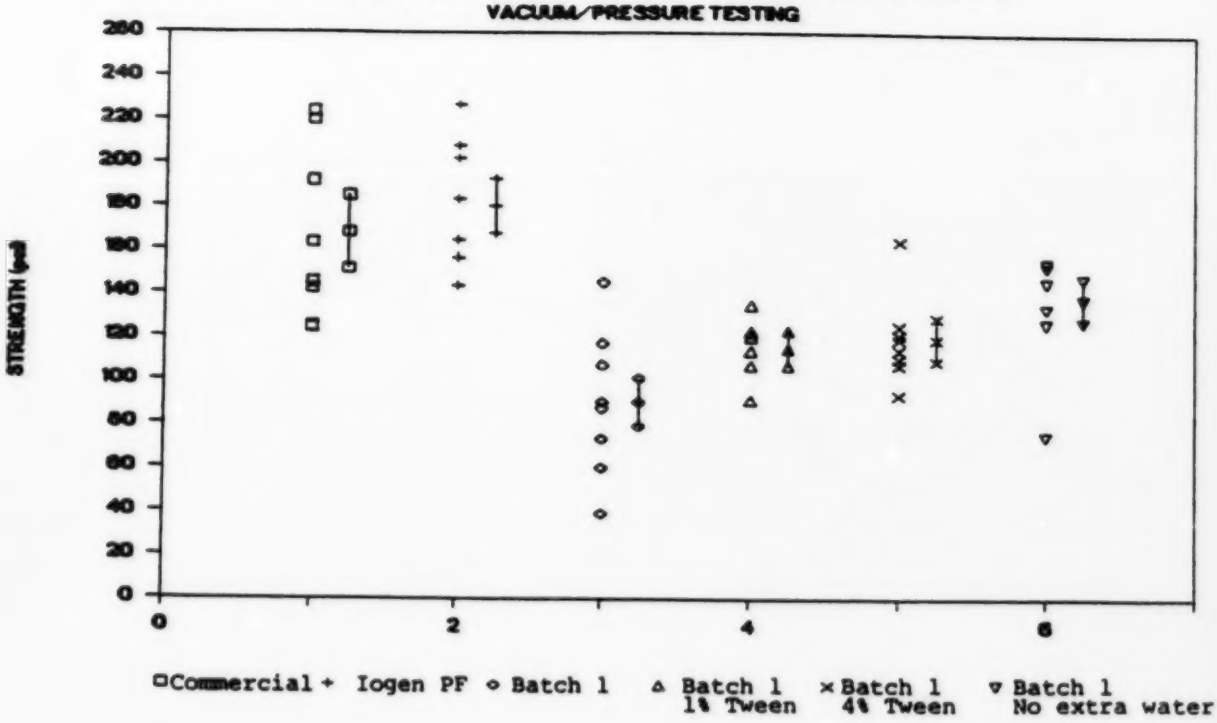


FIGURE 4-20: METHOXYL CONTENT OF ALKALI LIGNIN

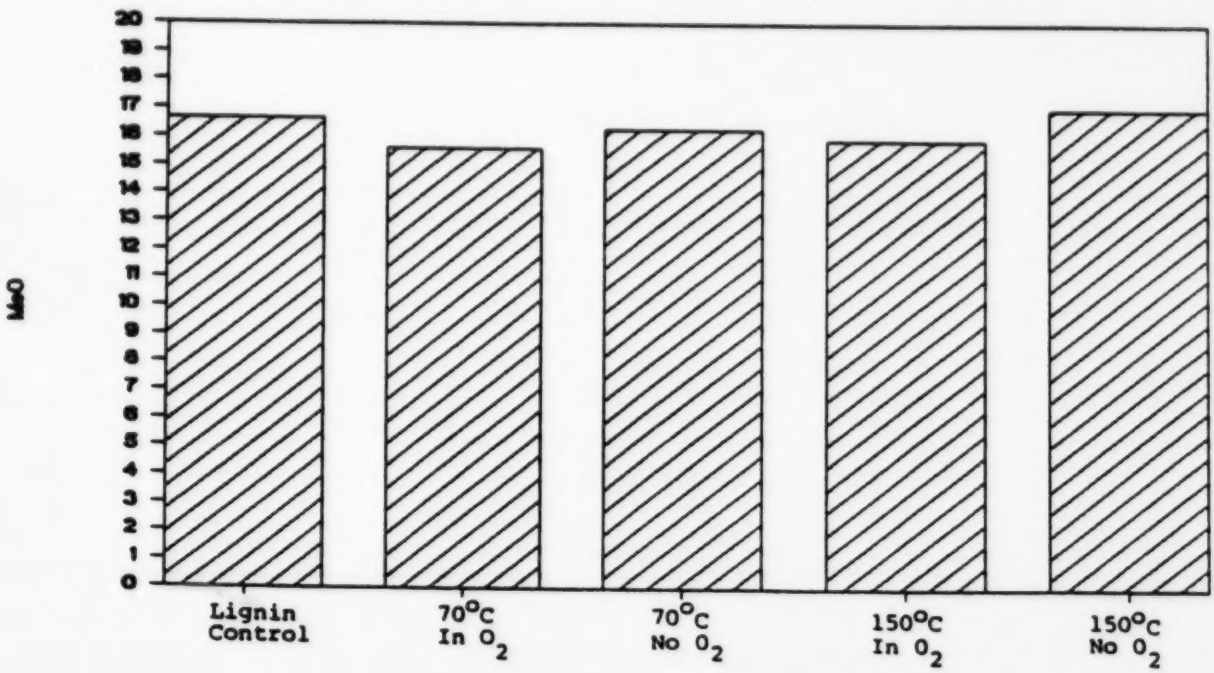


FIGURE 4-21: COMPOSITION OF ALKALI LIGNIN GLUES

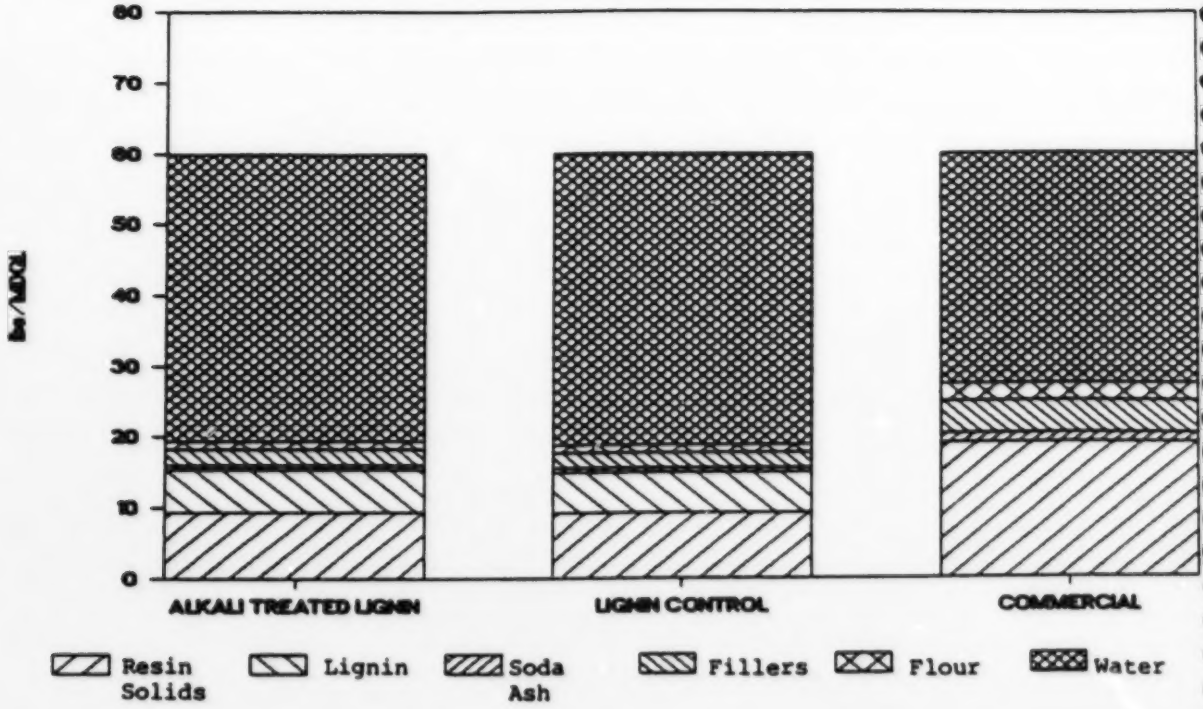


FIGURE 4-22: ALKALI TREATED LIGNIN GLUES

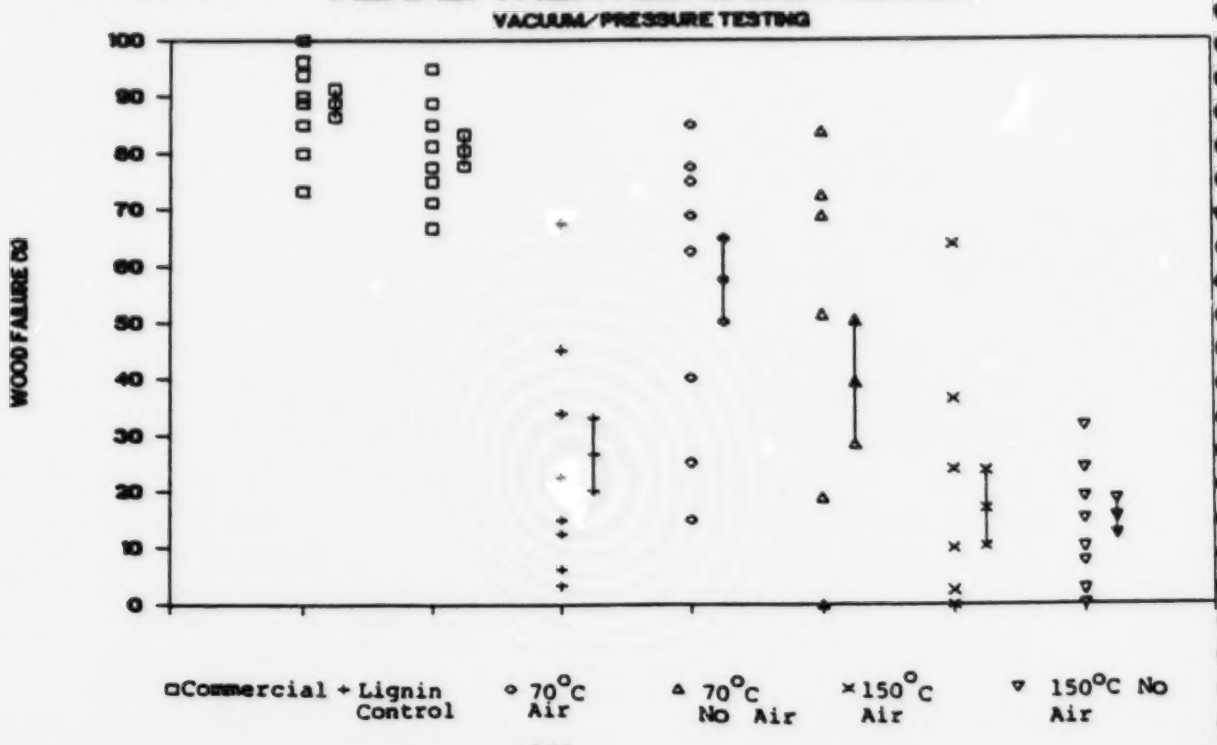


FIGURE 4-23:

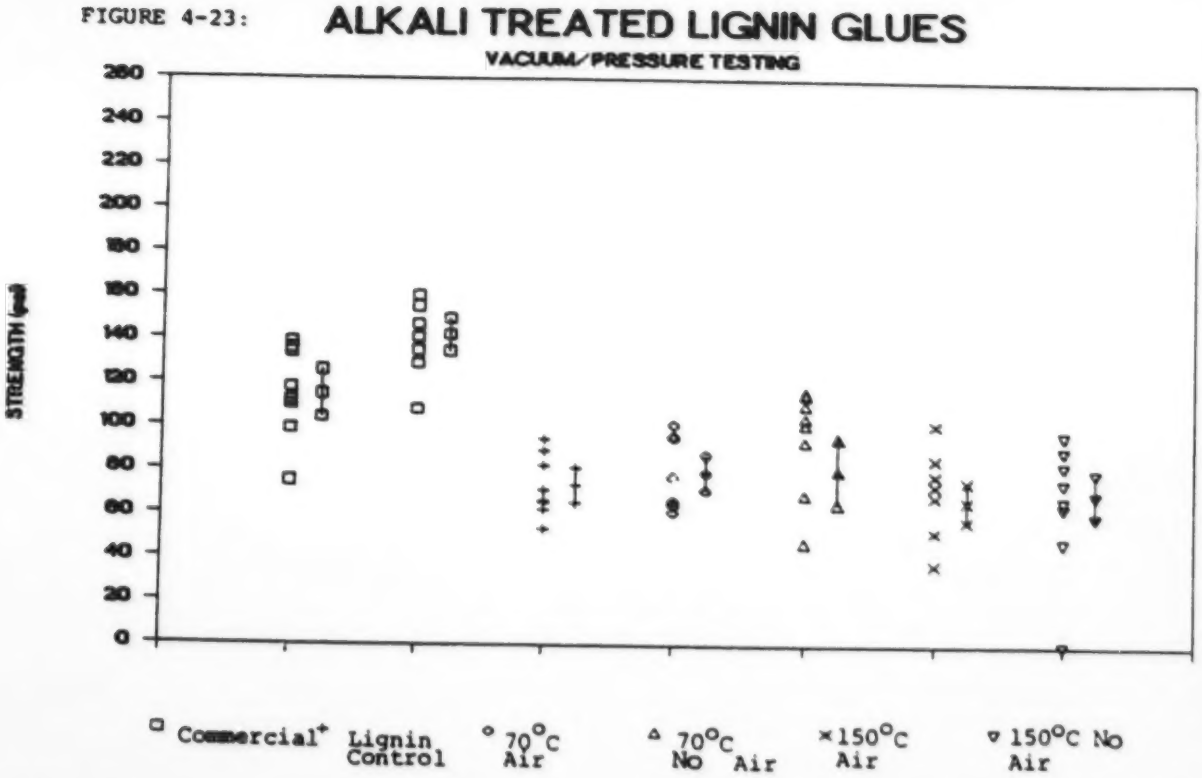

ALKALI TREATED LIGNIN GLUES
VACUUM/PRESSURE TESTING
STRENGTH (psi)
280
240
220
200
180
160
140
120
100
80
60
40
20
0
Commercial* Lignin Control
70°C Air
70°C No Air
150°C Air
150°C No Air

FIGURE 6-1: FREE FORMALDEHYDE STANDARD CURVE

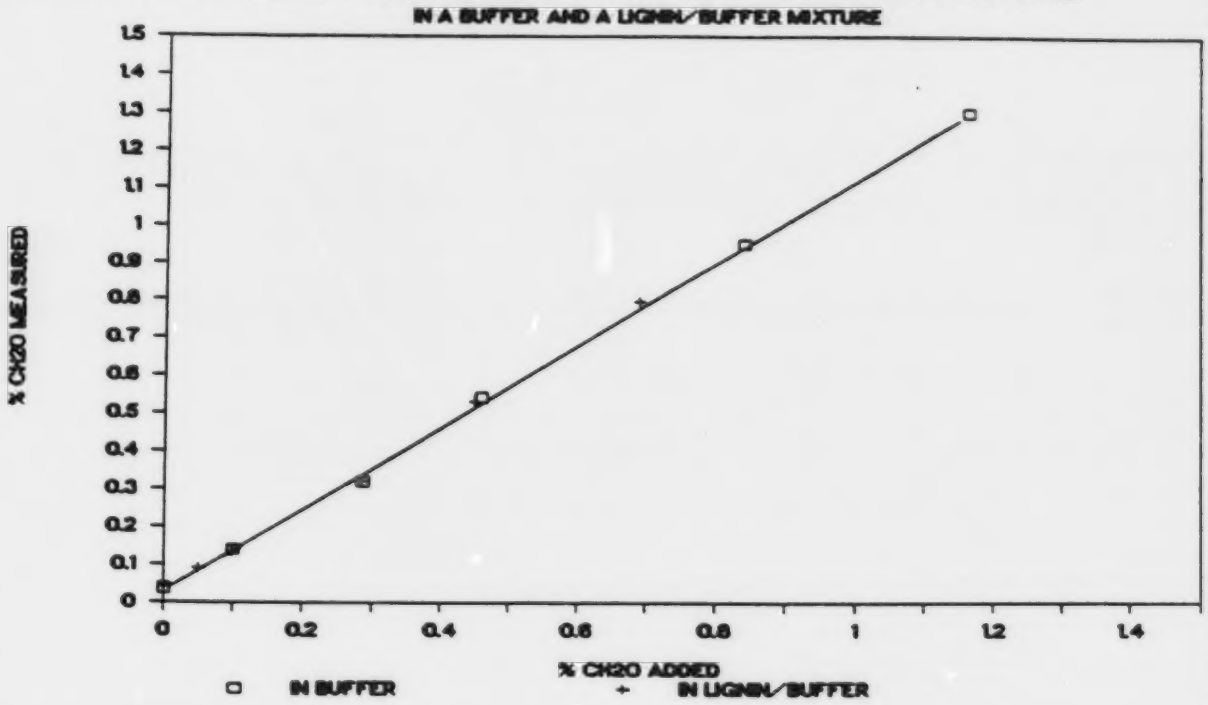


Figure 6-2: Formic Acid Standard Curve

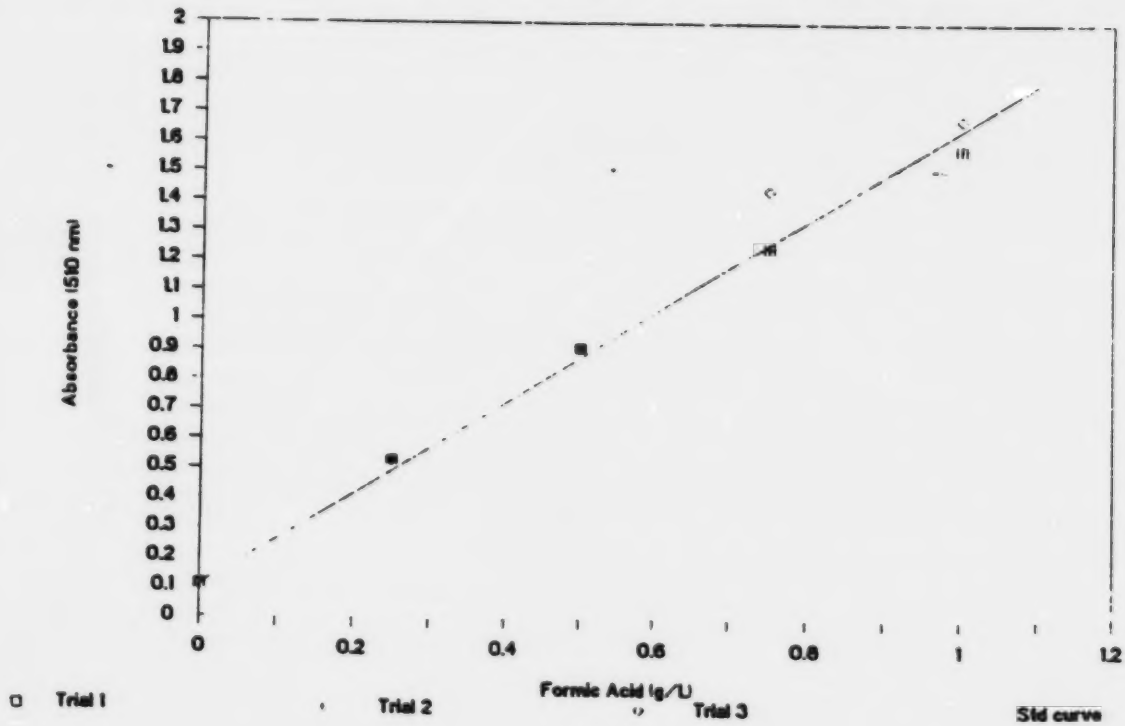


FIGURE 6-3: PHENOL/LIGNIN STANDARD CURVES

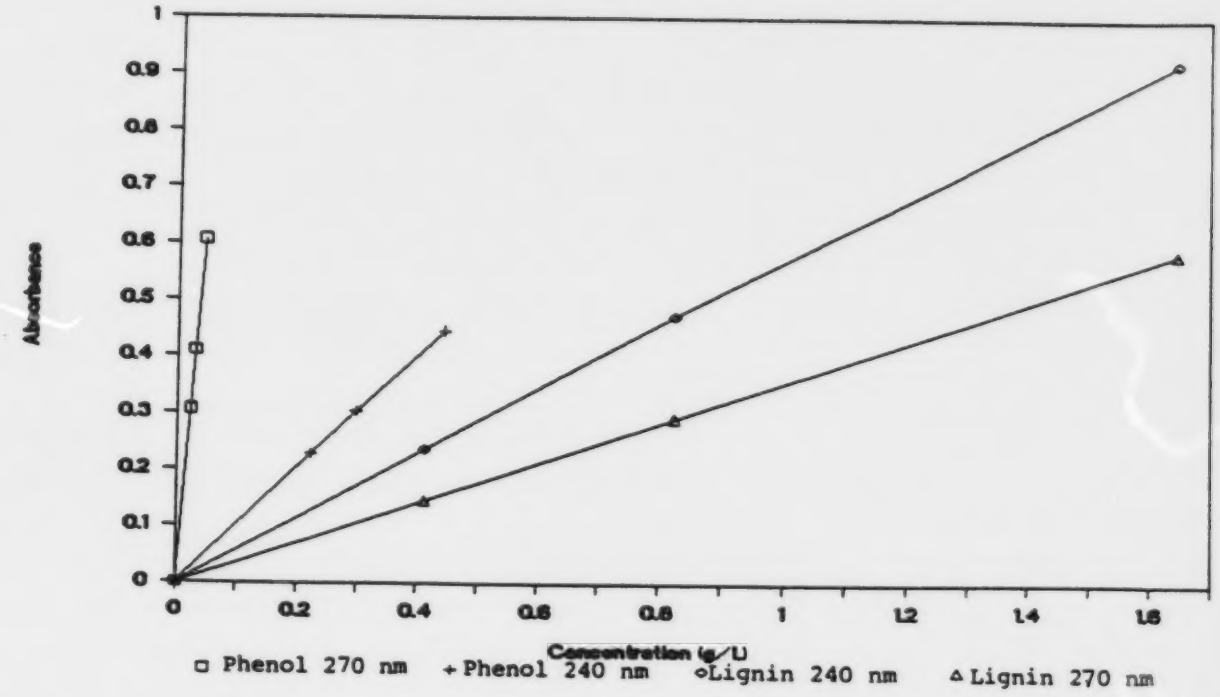


FIGURE 6-4: ADDED VS. MEASURED PHENOL (g/L)

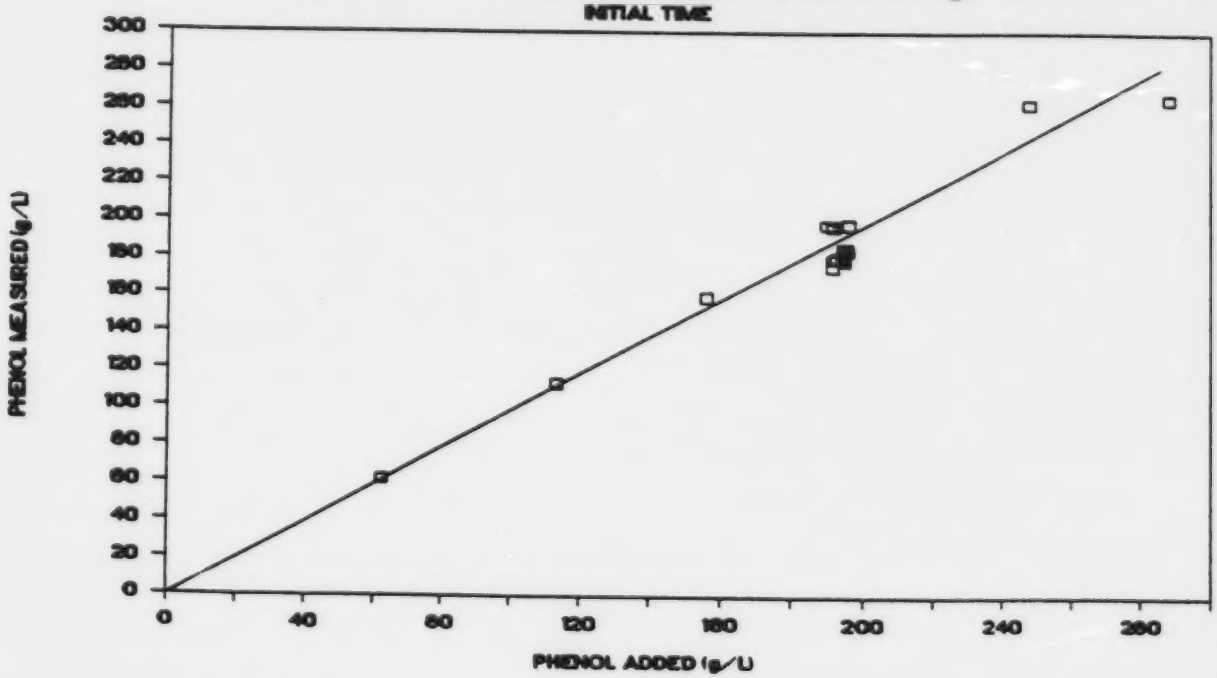


Table 6-1: GLUE FORMULATIONS WITH UM LIGNIN (Lbs/MDGL)

Douglas fir

	Control	% Substitution of PF Resin 21	51	70
Resin Solids	18.42	14.32	8.88	5.50
Soda Ash	1.31	1.03	0.64	0.40
Lignin	0.00	3.07	7.61	11.79
Cocob	2.99	2.35	1.46	0.90
RX-100	1.65	1.29	0.80	0.50
Flour	2.63	2.07	1.28	0.79
Water	33.00	35.86	39.33	40.12
Total	60.00	60.00	60.00	60.00

Poplar

	Control	% Substitution of PF Resin 23	52	70
Resin Solids	21.70	16.71	10.36	6.42
Soda Ash	1.23	1.21	0.75	0.46
Lignin	0.00	3.58	8.88	13.76
Cocob	5.14	2.74	1.70	1.06
RX-100	0.00	1.51	0.94	0.58
Flour	3.62	2.41	1.49	0.93
Water	38.31	41.84	45.88	46.80
Total	70.00	70.00	70.00	70.00

Spruce

	Control	% Substitution of PF Resin 21
Resin Solids	20.24	15.84
Soda Ash	1.39	1.10
Lignin	0.00	3.42
Cocob	1.58	1.24
RX-100	0.00	0.00
Flour	2.78	2.19
Water	36.86	39.55
Total	66.00	66.00

Table 6-2: PLYWOOD MANUFACTURING CONDITIONS

	Douglas Fir	Poplar	White Spruce
Glue Spread (Lbs/MDGL)	60	70	66
Number of Ply	3	3	3
Panels per Opening	2	2	2
Cold Press			
Pressure (psi)	180	75	195
Time (minutes)	5	6	4
Hot Press			
Temperature (^{o}C)	135	135	135
Initial pressure (psi)	185	150	200
Initial time (minutes)	1	3	4.5
Final pressure (psi)	165	112	--
Final time (minutes)	4	3	--

Table 6-3: GLUE COMPOSITIONS OF PAPER TEST GLUES (Lbs/MDGL)

	Control	% Substitution of PF Resin 13%	23%	36%	52%
Resin Solids	18.12	15.85	13.87	11.60	8.74
Lignin	0.00	1.68	2.94	4.91	7.39
Soda Ash	1.48	1.30	1.13	0.95	0.72
Cocob	5.75	5.03	4.40	3.68	2.77
Flour	4.90	4.29	3.75	3.14	2.36
Water	39.75	41.84	43.90	45.73	48.01
Total	70.00	70.00	70.00	70.00	70.00
% Solids	43.22	40.21	37.28	34.68	29.63

Table 6-4: COMPOSITION OF LIGNIN/RESIN COREACTED GLUES

	Lbs/MDGL on Douglas fir Commercial	Lignin/Resin
Resin Solids (excl. Lignin)	19.00	12.65
Lignin (in resin)	0.00	6.38
Soda Ash	1.36	0.74
RS100	1.60	0.88
Cocob	2.86	1.58
Wheat Flour	2.41	1.33
Water	32.77	36.44
Total	60.00	60.00

Table 6-5: COMPOSITION OF LIGNIN/RESIN GLUES

	Commercial	Lignin/PF	Iogen PF
Resin Solids (excl. Lignin)	20.08	13.84	20.08
Lignin (in resin)	0.00	6.24	0.00
Soda Ash	1.36	0.84	0.77
RX100	1.60	1.00	0.91
Cocob	2.86	1.78	1.63
Wheat Flour	2.41	1.49	1.37
Water	31.68	34.81	35.22
Total	60.00	60.00	60.00

Table 6-6: Specific Absorbances

Substrate	A° or A^{L} (240 nm) [A/(g/L)]	A° or A_{L} (270 nm) [A/(g/L)]
Phenol	0.980	13.440
Exploded Wood Lignin	0.518	0.282
Indulin AT	0.867	0.833
Reed Lignin	1.246	0.592
Hardwood SSL	21.500	8.838
Softwood SSL	24.975	11.036
Exploded Wood Lignin with catalyst	0.864	0.648

Table 6-7: COMPOSITION OF HYDROXYMETHYLATED LIGNIN GLUES

				Lbs/MDGL on Douglas fir				
	Commercial	Lignin Control	T	P	A	F30	F10	F0
Resin Solids	18.25	8.49	8.11	9.48	9.40	9.17	8.78	9.01
Soda Ash	1.30	0.60	0.58	0.67	0.67	0.65	0.62	0.64
RX100	1.54	0.71	0.68	0.80	0.79	0.77	0.74	0.76
Cocob	2.75	1.28	1.22	1.43	1.42	1.38	1.32	1.36
Wheat Flour	2.31	1.08	1.03	1.20	1.19	1.17	1.11	1.14
Lignin	0.00	7.21	5.21	5.03	5.76	5.21	4.66	4.65
Water	33.84	40.62	43.16	41.39	40.77	41.65	42.77	42.45
Total	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00

Table 6-8: COMPOSITION OF HM LIGNIN P/F RESIN GLUES

Lbs/MDGL on Douglas fir

	Commercial	HM Lignin P/F	Lignin Control
Resin Solids	18.57	12.89	9.25
Soda Ash	1.33	1.14	0.67
RX100	1.58	1.35	0.78
Cocob	2.82	2.41	1.40
Wheat Flour	2.37	2.03	1.18
Lignin'	0.00	5.82	5.82
Water	33.33	34.37	40.90
Total	60.00	60.00	60.00

' Includes reacted lignin or unmodified lignin

Table 6-9: COMPOSITION OF PHENOLATED LIGNIN GLUES

Lbs/MDGL on Douglas fir

	Commercial	Caustic Insoluble Phenolated Lignin	Caustic Soluble Phenolated Lignin	Lignin Control
Resin Solids	18.07	11.29	8.90	9.25
Soda Ash	1.30	0.81	0.63	0.67
RX100	1.53	0.95	0.75	0.78
Cocob	2.74	1.71	1.35	1.40
Wheat Flour	2.30	1.44	1.14	1.18
Lignin	0.00	9.81	7.74	5.82
Water	34.06	33.99	39.49	40.90
Total	60.00	60.00	60.00	60.00

Table 6-10: COMPOSITION OF PHENOLATED LIGNIN PF RESIN GLUES

First Set

(Lb/MDGL on Douglas fir)

	Commercial	Phenolated Lignin Batch 1	Phenolated Lignin Batch 2	Iogen PF	Lignin Control
Resin Solids (excl. Lignin)	18.75	13.15	13.15	18.72	9.21
Lignin (in resin)	---	5.56	5.56	---	5.29
Soda Ash	1.35	0.58	0.45	0.94	0.66
RX100	1.59	0.69	0.54	1.11	0.78
Cocob	2.84	1.23	0.95	1.99	1.39
Wheat Flour	2.39	1.04	0.80	1.67	1.18
Water	33.08	37.74	38.55	35.57	40.98
Total	60.00	60.00	60.00	60.00	60.00

Second Set

(Lb/MDGL on Douglas fir)

	Commercial	Phenolated Lignin Batch 1	Tween 1*	Tween 1*	Phenolated Lignin Batch 1 No Extra Water	Iogen PF	Lignin Control
Resin Solids (excl. Lignin)	18.74	13.35	10.59	12.29	14.50	20.26	9.08
Lignin (in resin)	--	5.59	4.43	5.14	6.07	--	5.84
Soda Ash	1.34	0.59	0.47	0.55	0.44	1.02	0.66
RX100	1.59	0.70	0.55	0.64	0.51	1.20	0.77
Cocob	2.84	1.25	0.99	1.15	0.93	2.15	1.39
Wheat Flour	2.39	1.05	0.83	1.45	0.77	1.81	1.17
Tween	--	--	1.64	0.46	--	--	--
Water	33.08	37.48	40.49	38.80	36.77	33.56	41.09
Total	60.00	60.00	60.00	60.00	60.00	60.00	60.00

* Tween 1 had 4% Tween added on Batch 1 resin
* Tween 2 had 1% Tween added on Batch 1 resin

Table 6-11: COMPOSITION OF ALKALI LIGNIN GLUES

Lbs/MDGL on Douglas fir

	Commercial	Caustic Treated Lignin Glues	Lignin Control
Resin Solids	18.92	9.31	9.11
Soda Ash	1.36	0.67	0.65
RX100	1.61	0.79	0.77
Cocob	2.87	1.41	1.38
Wheat Flour	2.41	1.19	1.97
Lignin	--	6.11	5.72
Water	32.83	40.52	41.20
Total	60.00	60.00	60.00